STUDIES IN THE ANALYTICAL CHEMISTRY OF TUNGSTEN

Thesis for the Degree of Ph.D.

Presented

by

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TABLE OF CONTENTS

INTRODUCTION

Tungsten occurs in nature mainly as tungstate associated with calcium, copper, iron, manganese and lead in minerals such as scheelite, wolframite and stolzite. It is employed chiefly as a constituent of alloys and steels for materials which are required to stand up to extremes of conditions. It may be necessary for the analyst to determine from traces to major amounts in ores, minerals and alloys, all containing numerous potentially interfering elements.

Traces and quantities of tungsten up to about 5% may most readily be determined instrumentally. Spectrographic and photometric procedures are most common, both the thiocynate - stannous chloride and the toluene-3:4-dithiol procedures being used in the latter. A more recent development is X-ray fluorescence spectrometry (1), and, with further advances, atomic absorption spectroscopy will probably yet be utilised (2). Both these methods are capable of giving rapid estimations of elements with increased selectivity. For quantities appreciably greater than 5%, the accuracy obtainable by all the methods mentioned becomes somewhat limited.

For major amounts of tungsten a gravimetric or volumetric method is necessary, the former finding general favour. Titrimetric methods have not come into common usage since, as was stated in a review (3), they are by no means selective and considerable doubts exist as to their accuracy. Most such methods involve reduction of tungsten^{VI} to a lower valence state and subsequent titration with a standard oxidant. Tungsten being polyvalent, it is by no means easy to ensure a definite reduced form. A recent example of this is Perrier's method (4), where a fractional valence

state was employed empirically. Titrations involving precipitating agents have also been described (3). Either a substance containing tungsten has been precipitated, separated and dissolved, and a constituent determined, or a precipitant for tungstate has been used as a titrant, in conjunction with an adsorption indicator for locating the equivalence-point.

The earliest gravimetric determinations of tungsten were based on precipitation of insoluble tungstates of metals such as calcium, barium, mercury and lead. Mercurous nitrate recommended for use by Berzelius in 1816 is still used to some extent (5), as after a single precipitation ignition yields tungstic oxide. Chloride must be absent and the ignition of large precipitates of mercury salts is reputedly a risky operation (6).

Straightforward hydrolytic precipitation of tungstic acid in mineral acid solution has also been used. Here, loss due to incomplete precipitation can be marked and the method has fallen into abeyance. The most commonly reported methods involve completion of precipitation by the addition of an organic base, usually after the bulk of the tungstic acid has been hydrolytically precipitated. No definite complex is formed, the base merely forming an adsorption complex with tungstic acid (7). The mixed precipitate is then ignited to give tungstic oxide. Numerous bases, all functioning in the same way, have been recommended for this purpose and have been listed by Claeys (5), and Clercq and Duval (8). While benzidine, β-naphthoquinoline and α-benzoin oxime have found some measure of acceptance, the reagent most commonly used is cinchonine. That this reagent, first suggested over sixty years ago (5), is still in use to-day is not so much an indication of the satisfactory nature of the method based on its use,

but rather a measure of the difficulty of effecting an improvement.

Tannin, which was recommended by Schoeller and Jahn (9) for use along with cinchonine, is particularly useful for determining small amounts of tungsten. Alkali salts appreciably delay the precipitation by cinchonine, especially where only a few milligrams of tungsten are present. Very thorough washing of the separated precipitate is also necessary with consequent risk of loss. Tannin forms a partly colloidal adsorption complex with tungstic acid which is not completely precipitated. Cinchonine, a base which gives insoluble tannin compounds, is used to flocculate this material, the process being assisted by the presence of alkali salts. To-day, milligram amounts of tungsten are more likely to be determined photometrically.

All of the precipitates obtained in gravimetric procedures are liable to be contaminated and require to be examined for impurities. Silica usually accompanies tungstic acid but is readily eliminated by volatilisation as silicon tetrafluoride. Iron is present in most tungsten-containing materials and an appreciable amount is almost invariably found in the precipitate. Reprecipitation can be avoided and iron corrected for by fusing the crude tungstic acid with sodium carbonate, extracting sodium tungstate with water, and separating and determining residual ferric oxide.

Other potential impurities are phosphorus, arsenic, boron and germanium, which can form heteropoly acids with tungsten. To overcome the interference of phosphorus (10) and arsenic (11), Lambie recommended formation of the tannin complex in an alkaline solution with subsequent acidification and addition of the base. Heteropoly acids are not formed under these

conditions.

None of the existing methods can be applied directly in the presence of much molybdenum as considerable coprecipitation occurs (12). A fusion and reprecipitation are usually necessary. Alternatively as in the British Iron and Steel Research Association method (13), molybdenum is determined colorimetrically and a correction applied. Chromium, tantalum and niobium may also contaminate the precipitate and require to be corrected for.

In order to improve on the classical method, attempts have been made to precipitate tungsten as a definite complex. So far acridine (14) and oxine (15) have been recommended but thermogravimetric analyses by Clercq and Duval (8) have shown that these are unsatisfactory. Duval (16) mentions, however, that definite complexes can be formed by amines with tungstophosphate and tungstosilicate although he states that, unlike molybdenum, tungsten does not form heteropoly acids quantitatively and instantaneously.

In the present work it was intended to study the gravimetric determination of tungsten and attempt to form a weighable tungstate complex. By having all the tungsten present in a definite soluble form before adding a precipitant, it was hoped that it would not be necessary to examine the precipitate subsequently obtained for impurities. For this purpose the heteropoly complexes appeared most suitable as the acids are soluble in mineral acid solutions and can be precipitated by certain inorganic cations and complex cations, as well as by organic bases. Silicon, phosphorus and arsenic are the commonest elements associated with formation of soluble heteropoly acids containing tungsten. Conversion of tungsten to

tungstosilicic acid might be accompanied by objectionable production of silicic acid. Since silicon and arsenic can easily be eliminated by volatilisation with hydrofluoric and hydrochloric acids, respectively, and phosphorus cannot, 12-tungstophosphoric acid was selected for study.

Tungstophosphoric acid is a recognised precipitant for detection and determination of alkaloids and other organic substances containing basic nitrogen (17), (18). Amine complexes of cobalt, nickel, copper and chromium also form insoluble products with 12-tungstophosphoric acid but these precipitates are usually of indefinite composition because they are formed in solutions of low acidity where partial degradation of the heteropoly acid occurs (19).

Almost all the information available refers to determination of bases with 12-tungstophosphoric acid. Roberts (20), however, has used the ferrous o-phenanthroline complex of 12-tungstosilicic acid for determining small amounts of both silicon and tungsten. It is not known how he formed the heteropoly acid and avoided interference from excess tungstic acid or silicic acid. Simpson and his co-workers (21) showed that in the presence of excess phosphate, tungstate could be precipitated from an acidified solution by means of cinchonine, presumably as cinchonine 12-tungstophosphate, since the ignition product corresponded to $P_2O_5.24WO_3$. Lambie proved that 12-tungstoarsenate was similarly precipitated by cinchonine (11) and that 12-tungstophosphate was precipitated by ammonium chloride solution (10). No attempt was made to utilise these precipitations as analytical methods for tungsten.

The aim of the present work was firstly, to study the precipitation

of 12-tungstophosphoric acid with various reagents with a view to determination of tungsten as a complex tungstophosphate, the investigation being restricted to determination of large amounts of tungsten; secondly, to examine the influence on the determination of tungstophosphate of other elements commonly associated with tungsten; thereafter, to find out how best to effect formation of tungstophosphoric acid and determine it in their presence; and finally, to analyse a few selected materials for tungsten.

APPARATUS

Special apparatus designed for particular operations is described in the text.

Pipettes, burettes and volumetric flasks: Grade A or B, calibrated when necessary by weighing the volume of water delivered or contained.

Sintered filtering crucibles: Royal Berlin porcelain 1A2, 25 ml. Royal Worcester porcelain M2/4, 6 ml. Glass crucibles, No. 4, 20 ml.

Platinum ware: Crucibles of 6, 10, and 25 ml capacity with fitting lids.

Plastic ware: Polythene beakers and covers. Polythene bottles for storing solutions of hydrofluoric acid, fluorides and sodium hydroxide. Polyvinyl chloride tubing for a chromatographic column in which hydrofluoric acid was used and for a measuring cylinder. Polytetrafluoroethylene beakers, with covers and stirring rods, for disintegrations of materials involving use of hydrofluoric, nitric and hydrochloric acids.

Balances and weights: Stanton aperiodic weight-loading analytical balance, model AD2, sensitive to 0.1 mg. Bunge microbalance, sensitive to 0.001 mg for weighings in C, H and N determinations. Weights were calibrated at intervals.

Miscellaneous: Thermostatically controlled oven capable of giving temperatures over 200°C.

Electrically heated hot-plates, some with magnetic stirrers. Stirrer bars 2.5 cm in length.

Electric bunsens with simmerstat control, calibrated by thermocouple where necessary.

Muffle furnace, electrically heated and fitted with thermocouple.

Aluminium heating blocks, diameter and height 3 inches, with cavities suitable for platinum crucibles.

Unicam SP500 spectrophotometer.

Cambridge pH meter.

Centrifuge, suitable for tubes up to 15 ml.

REAGENTS

Sodium tungstate, $Na_2WO_4.2H_2O$: B.D.H., AnalaR grade.

12-Tungstophosphoric acid: B.D.H., AnalaR grade.

18-Tungsto-2-phosphoric acid: prepared according to the method of Kehrmann (22).

Tungstic oxide: Matthey "Specpure", 99.995%.

Tungsten powder: Johnson, Matthey & Co. Ltd. 99.9% minimum purity, 5-10 microns.

Iron powder: Matthey Iron Sponge, spectrographically standardised.

Tri-n-butylamine: B.D.H., dried over potassium carbonate and purified by vacuum distillation twice, the colourless fraction boiling between 83 and 85°C at 10 mm pressure being finally collected. The material was redistilled every two months or when a yellow coloration appeared.

Toluene-3:4-dithiol: The zinc salt (Hopkin and Williams, Ltd.), hereinafter called "dithiol", was used for all tests.

Cellulose powder: Whatman Ashless, Standard Grade.

Sodium hydroxide solutions were made up in plastic beakers and stored in polythene bottles in order to avoid introduction of silica.

Distilled water from a copper still was used throughout.

Other reagents were, when available, of recognised analytical quality.

EXPERIMENTAL

1. The Precipitation of 12-Tungstophosphoric Acid - The Use of Inorganic Precipitants

Lambie (10) showed that tungstate acidified in the presence of excess phosphate could be precipitated as ammonium tungstophosphate. Despite a large excess of ammonium chloride, recovery of tungsten was less than 99% due, in part at least, to the slight solubility of ammonium tungstophosphate.

Potassium, thallium^{I} and caesium salts also give insoluble precipitates with 12-tungstophosphoric acid. Caesium salts were considered too expensive for use in an analytical method, but since this work was done a paper on the determination of caesium as a tungstophosphate has been published (23).

A comparison was made of ammonium, potassium and thallium^{I} salts with regard to the precipitation of tungstophosphate from varied concentrations of hydrochloric and nitric acid solutions. Qualitatively, precipitation was found to be best effected at acid concentration less than 0.5N. Thallium nitrate precipitated tungstophosphate most readily, although precipitation of small amounts from the nitric acid solution was slow.

Quantitative experiments were attempted with thallium nitrate solution as precipitant. Since 12-tungstophosphoric acid has a variable water content, rendering it unsuitable as a standard for determination of tungstophosphate, it was provisionally assumed that 12-tungstophosphoric acid would be quantitatively formed by acidifying a solution containing sodium tungstate and sodium phosphate.

25 Ml of solution containing 100 mg of tungsten as tungstate and 8.5 mg of phosphate (PO4) were acidified and made 0.4N in nitric acid.

10 Ml of 0.1M thallous nitrate solution were added slowly to the hot solution. After digestion for 2 hours, the precipitate was separated, dried at 140°C and weighed. Precipitates obtained were fine and colloidal despite variation of the conditions, including addition of electrolytes to assist coagulation. It was uncertain whether formation of thallium tungstophosphate was complete as collection of the precipitate was unsatisfactory. Ignition residues were about 7% low for $3Tl_2O.P_2O_5.24WO_3$. Corresponding amounts of tungsten were estimated to be present in the filtrates by means of the dithiol reaction (Appendix p.95).

As preliminary experiments were not particularly successful, and contamination of the precipitates by other metal ions appeared probable, due to the cation exchange properties of the salts of the heteropoly acids (24), the approach was abandoned in favour of precipitation with organic reagents.

2. The Precipitation of 12-Tungstophosphoric Acid - The Use of Organic Precipitants

Using 12-tungstophosphoric acid as precipitant, Kahane and Kahane (17) obtained well-defined anhydrous compounds at 100°C from a large number of primary, secondary and tertiary amines, arylamines, amino acids, quaternary ammonium salts and heterocyclic bases. With multibasic compounds, the composition of the products was affected to an appreciable extent by the conditions of precipitation. Use could be made of the weights of the dried precipitates and the ignited residues to obtain a measure of the molecular weights of simple bases. For maximum precipitation of these, Jean (18) found that there was an optimum acidity, usually between pH 3 and pH 1, but for a series of homologues this optimum became less marked as the molecular weight increased. For alkaloids, maximum precipitation occurred at an increasingly higher acidity as molecular weight increased. For cinchonine 0.5 to 1N was best.

A study was first made of the precipitation of 12-tungstophosphoric acid from mineral acid solution with a number of organic bases in order to select the best precipitant.

(i) Preliminary tests on precipitation of tungstophosphate.

10% solutions of various organic basic substances and quaternary ammonium salts, which were not specially purified, were prepared in dilute hydrochloric acid or in water. A few drops of each solution were added, with stirring, to 2 ml of a hot solution containing 2 mg of sodium tungstate, 0.8 mg of disodium hydrogen orthophosphate and sufficient hydrochloric acid to make the solution 0.1 or 1.5N. Each precipitate was spun in a centrifuge,

and a portion of the supernatant solution was tested for tungsten with dithiol. Promising reagents were quinoline, isoquinoline, 2:4-dimethylquinoline, 8-hydroxy- and 5:7-dibromo-8-hydroxyquinoline, benzylphenyldimethylammonium chloride, cetyltrimethylammonium chloride, 4:4'-tetramethyldiaminobenzophenone, tri-n-butylamine and cinchonine. The degree of precipitation with diethylenetriamine, triethylenetetramine, triethanolamine, tetraethylammonium hydroxide, piperazine hydrate and 2-chloroquinoline was unsatisfactory. With some of the former group of substances, quantitative experiments were similarly made on larger amounts of solutions approximately N in hydrochloric acid and containing 200 mg of sodium tungstate. Precipitates were collected, dried at 105°C and weighed. Portions were then ignited to tungstophosphoric oxide and weighed. The ratio of the molecular weights calculated for the products obtained at 105°C to those expected for certain anhydrous complexes are shown in Table I; these results suggested that definite complexes were formed, excess of molecular weight over that expected being accounted for by water of hydration or contamination by the reagent.

TABLE I

RATIOS OF MOLECULAR WEIGHTS CALCULATED FROM EXPERIMENTAL RESULTS TO THOSE EXPECTED FOR VARIOUS COMPLEXES

	Formula for anhydrous complex	Molecular weight from experiment / Molecular weight expected
Quinoline	$(C_9H_7N.H)_3PW_{12}O_{40}$	1.02
Cetyltrimethylammonium chloride	$(C_{19}H_{42}N)_3PW_{12}O_{40}$	1.06
5:7-Dibromo-8-hydroxyquinoline	$(C_9H_5Br_2ON.H)_3PW_{12}O_{40}$	1.05±0.02
Cinchonine	$(C_{19}H_{22}ON_2.H_2)_3(PW_{12}O_{40})_2$	1.03
8-Hydroxyquinoline	$(C_9H_7ON.H)_3PW_{12}O_{40}$	1.01
2:4-Dimethylquinoline	$(C_{11}H_{11}N.H)_3PW_{12}O_{40}$	1.01
Tri-n-butylamine	$[(C_4H_9)_3N.H]_3PW_{12}O_{40}$	1.04

Solubility losses were about 1% for all reagents except quinoline, for which the loss was greater. Cetyltrimethylammonium chloride formed extremely slow-filtering precipitates, and 5:7-dibromo-8-hydroxyquinoline formed sticky precipitates that changed markedly in appearance when set aside. The complexes formed with 8-hydroxyquinoline and cinchonine absorbed moisture. The last four reagents in Table I were also applied to the determination of 5-mg amounts of tungsten in 100 ml of solution; yields were promising. Tri-n-butylamine, which formed easily filterable precipitates that did not adhere to glassware, was selected for further experiments, in preference to the much more expensive 2:4-dimethylquinoline. For comparison, a few experiments were also made with cinchonine. These will be briefly described at the appropriate places.

(ii). The precipitation of tungstophosphate by tri-n-butylamine

A standard solution of tungstate was prepared from anhydrous sodium tungstate, the tungsten content of which was checked against that of "Specpure" tungstic oxide as reference standard. Hydrated sodium tungstate was dried to constant weight at 300 to 400°C in a muffle furnace. Weighed portions of ignited tungstic oxide were converted to sodium tungstate by fusion with sodium carbonate. In the solutions therefrom and in solutions prepared from weighed amounts of anhydrous sodium tungstate, tungsten was determined under identical conditions by the classical cinchonine procedure (25). Anhydrous sodium tungstate was found to contain 100.1% of its theoretical tungsten content and sodium tungstate dihydrate 100.2% Appropriate corrections were afterwards applied in all critical experiments.

TABLE II

EFFECT OF HEATING TRI-n-BUTYLAMMONIUM TUNGSTOPHOSPHATE DERIVED FROM 500 MG OF TUNGSTEN

500 mg of tungsten = 779 mg of $[(C_4H_9)_3N.H]_3PW_{12}O_{40}$ = 647 mg of $P_2O_5.24WO_3$

Experiment No.	Weight of precipitate after heating at - 105°C for 1 hour, mg	150°C for 45 minutes mg	200°C for 1 hour, mg	200°C for 3 hours, mg	800°C for 1 hour, mg	Amount of tungsten found in filtrate mg
Filtration after 1 hour -						
1	783	782	777, 777	777	647	0.5
2	784	783	778, 778	778	647	0.1
3	807	-	784, 780	778	648	n.d.
Filtration after 18 hours -						
4	797	796	782, 778	777	645	0.1
5	-	-	779*, 778*	777†	-	0.1
6	-	-	781*, 779*	776†	-	0.8

* Heated at 215°C for 1 hour.

† Heated at 215°C for 18 hours.

A few experiments were made to determine the degree of completeness of precipitation and the composition of precipitates. To 240 ml of solution containing 0.5 g of tungsten, as sodium tungstate, and 0.32 g of disodium hydrogen orthophosphate were added 10 to 11 ml of 6N hydrochloric acid. To the boiling solution, 25 ml of a 2% w/v (3% in experiment No. 3, see Table II) solution of tri-n-butylamine in 0.25N hydrochloric acid were added dropwise, with stirring. The mixture was digested at its boiling-point for 15 minutes and cooled in an ice-water mixture for 1 hour or left overnight. The precipitate was then collected in a sintered-porcelain crucible and washed, first with an ice-cold 0.5% solution of tri-n-butylamine in 0.25N hydrochloric acid and finally with a little water. Heating was effected as indicated in Table II, in which all figures have been adjusted to be equivalent to exactly 0.5 g of tungsten. Weighed amounts of precipitates were transferred to platinum crucibles for ignition in order to avoid permanent contamination of filtering crucibles. Results were calculated to refer to ignition of the complete precipitate.

The results in Table II indicatedessentially complete precipitation of tungsten and ultimate formation of 12-tungstophosphoric oxide, andconfirmed the observations of Simpson and his co-workers (21) and of Lambie (10). Precipitates heated at 105 to 150°C gave erratic results, and a temperature above 200°C was necessary for removing a variable amount of impurity, supposedly a tri-n-butylammonium salt. In experiments Nos. 5 and 6, precipitates were heated immediately at 215°C to expedite removal of the impurity, but removal of the last traces was still slow and there was probably slight decomposition of the precipitate; this became noticeable

VARIATION IN WEIGHT PER 100 mg OF PRECIPITATE

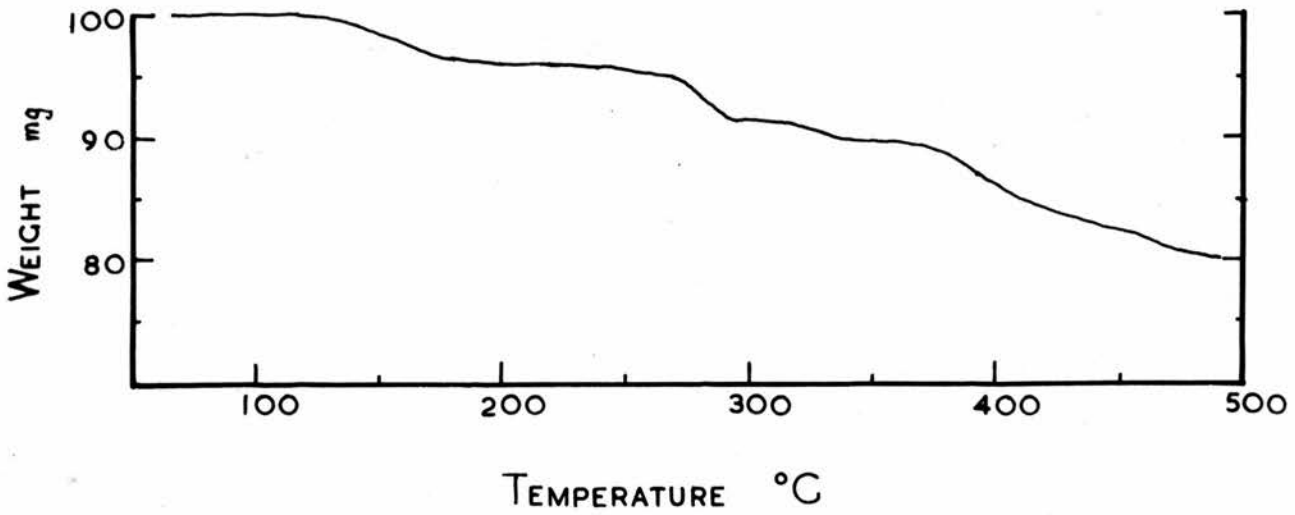

Figure 1.

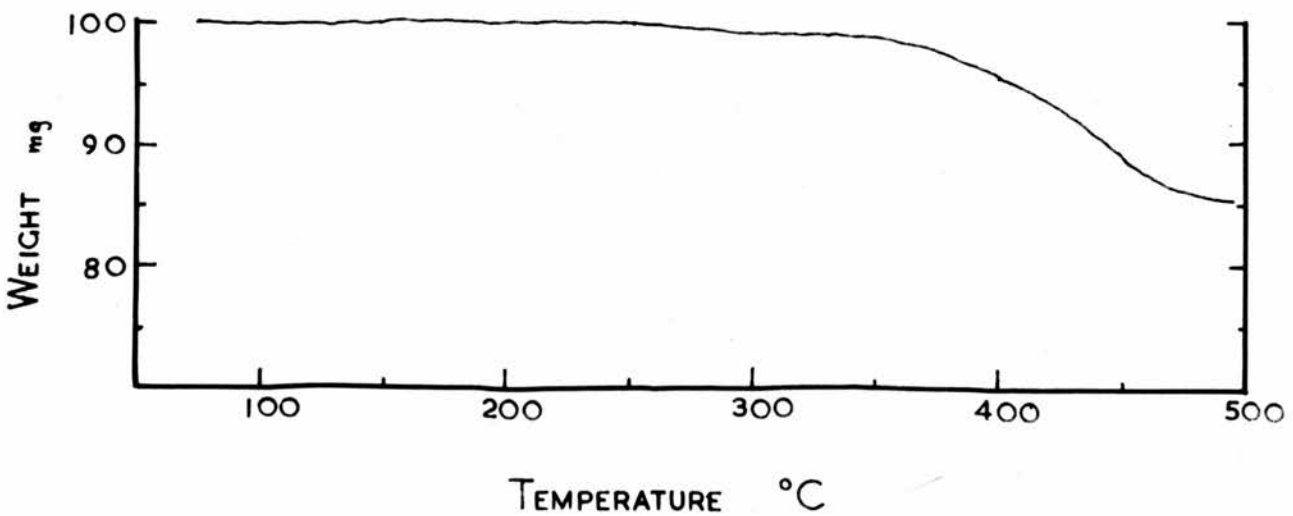

Figure 2.

at 250°C, the loss being 2 mg per hour.

Portions of the precipitate formed in experiment No. 3, in which the product obtained after heating at 105°C was significantly heavier, were utilised for several tests. A 123-mg sample was heated in a Stanton recording thermobalance, and the results are shown in Fig. 1. For weight constancy, a temperature between 195 and 220°C was indicated. Heating for 2 hours at 210°C was adopted in subsequent experiments. Although the initially white precipitates might become slightly discoloured or blackened at the edges, no important weight change appeared to be involved. In other 60-mg portions of precipitate, 1.39 and 1.40% of nitrogen were found by the Kjeldahl procedure (Appendix p. 98) under conditions in which tri-n-butylamine gave theoretical results for nitrogen. $[(C_4H_9)_3N.H]_3PW_{12}O_{40}$ contains 1.22% of nitrogen. The excess of nitrogen was equivalent to 24 mg of the amine or 29 mg of its hydrochloride per 500 mg of tungsten; the recorded weight loss of the precipitate between 105 and 200°C was of this order.

Amine complexes that had been cooled over calcium chloride absorbed 0.25% of water when exposed to an atmosphere of 50% relative humidity. Crucibles should therefore be cooled in a desiccator. Insufficient attention was paid to this matter in the experiments in Table II.

(iii). The precipitation of tungstophosphate by cinchonine.

The above procedure was also carried out with 25 ml of a 2.5% w/v solution of cinchonine in 0.25N hydrochloric acid as precipitant. 500 Mg of tungsten yielded 763 mg of precipitate heated at 105°C and cooled over calcium chloride, and 649 mg heated at 800°C. 500 Mg of tungsten=753 mg of

$(C_{19}H_{22}ON_2.H_2)_3(PW_{12}O_{40})_2$=647 mg of $P_2O_5.24WO_3$. The precipitate at 105°C was hygroscopic and probably contained some water. 1.8% was further absorbed on exposure to an atmosphere of 50% relative humidity. Contamination by excess reagent, which would be less readily removed than tri-n-butylamine, also probably occurred. A 150-mg portion of the precipitate was heated in a Stanton recording thermobalance and the results are shown in Fig. 2. Weight constancy was obtained from 100 to 250°C, above which there was a continuous loss in weight. In another 60-mg portion of precipitate 1.34% of nitrogen was found, $(C_{19}H_{22}ON_2.H_2)_3(PW_{12}O_{40})_2$ requiring 1.27%. These observations indicate that the precipitate was contaminated with a little cinchonine which apparently could not be removed without breaking down the complex.

(iv). The formation of 12-tungstophosphoric acid from sodium tungstate and phosphate

It was next necessary to show that 12-tungstophosphoric acid was indeed formed in the experiments described above. Tungsten in 25-ml portions of a filtered solution of 12-tungstophosphoric acid, containing approximately 0.8% of tungsten, was determined as the tri-n-butylammonium complex in presence of 0.25N hydrochloric acid, both with and without extra phosphate added as orthophosphoric acid. In further portions, the complex acid was fully degraded (pH>9) with a small excess of sodium hydroxide solution, more phosphate, as disodium hydrogen orthophosphate, was added, if desired, the solution was acidified with sufficient hydrochloric acid to make the free acid 0.25N and tungsten was precipitated as before. The results are shown in Table III, from which it can be seen that no marked difference existed

between determinations made directly with 12-tungstophosphoric acid and those made after degradation and re-formation of tungstophosphoric acid when additional phosphate was added after degradation. As there was no apparent necessity to use a minimum amount, the effect of less than a ten-fold excess was not examined. The filtrate in experiment No. 3 contained 0.3 mg of tungsten; the filtrates in the other experiments each contained <0.2 mg of tungsten.

TABLE III

WEIGHTS OF TRI-n-BUTYLAMMONIUM TUNGSTOPHOSPHATE OBTAINED FROM SIMILAR PORTIONS OF 12-TUNGSTOPHOSPHORIC ACID SOLUTION

Approximately 200 mg of tungsten = 8.5 mg of phosphate (as PO_4)

Experiment No.	Amount of phosphate present, as PO_4, mg	Amount of precipitate obtained, mg	Conditions
1	8.5	311.3	Direct precipitation
2	85	311.7	
3	8.5	312.7	Solution made alkaline and slowly re-acidified
4	85	311.4	
5	85	311.3	Solution made alkaline and rapidly re-acidified

The precipitates from experiments Nos. 1 and 2 were ignited and fused with sodium carbonate, and phosphate in the fusion products was determined spectrophotometrically as vanadomolybdophosphate at 440 mμ (Appendix p. 96). The amounts of phosphorus found in 311 mg of precipitate were 2.88 and 2.90 mg, and the same amounts of precipitate obtained from tungstate plus phosphate gave 2.90 mg. The required amount is 2.81 mg.

(v). Procedure for the determination of tungstophosphate as tris(tri-n-butylammonium) 12-tungstophosphate

Tri-n-butylammonium chloride solution:- A 2% w/v solution of tri-n-butylamine was prepared by shaking the amine with just enough diluted hydrochloric acid to neutralise it.

Tri-n-butylamine wash solution:- A 0.1% w/v solution in 0.1N hydrochloric acid was used.

Method:- To about 50 ml of solution containing 10 to 200 mg of tungsten, as sodium tungstate, and at least 85 mg of phosphate as disodium hydrogen orthophosphate, 6N hydrochloric acid was added gradually with stirring until the pH was about 2, followed by 4 ml of excess acid. The solution was diluted to 100 ml with water and heated almost to its boiling point. 10 Ml of tri-n-butylamine reagent were added with stirring and the solution was kept hot for 15 minutes or until the precipitate had coagulated. The beaker of solution was cooled in an ice-water mixture if filtration had to be carried out after 1 hour, or set aside overnight in a cool place. The mixture was filtered through a fine-pore, porcelain or glass, filtering crucible and the precipitate washed with a minimum amount of cold tri-n-butylamine wash solution and then a little cold water. The precipitate was heated for 2 hours at 210°C, cooled in a desiccator and weighed.

After numerous experiments had shown that the precipitates were weight-constant after 2 hours' heating, weight-constancy was only checked at infrequent intervals.

TABLE IV

EFFECT OF DIFFERENT CONDITIONS ON DETERMINATION OF TUNGSTOPHOSPHATE WITH TRI-n-BUTYLAMINE

200 mg of tungsten = 8.5 mg of phosphate (as PO_4) = 50 mg of tri-n-butylamine

Amount of tungsten taken, mg	Amount of phosphate taken as PO_4, mg	Hydrochloric acid present N	Amount of tri-n-butylamine used, g	Weight of precipitate obtained - at 105°C mg	Weight of precipitate obtained - at 210°C mg	Amount of tungsten found, mg
Solution set aside for 1 hour before filtration -						
200.0	85	0.25	0.2	314.0	311.3	199.9
				313.7	311.1	199.8
10.0	85	0.25	0.2	15.9	15.4	9.9
				15.8	15.4	9.9
200.0	17	0.25	0.2	314.1	309.8	198.9
	680	0.25	0.2	312.7	309.8	198.9
	85	0.25	0.1	310.8	310.4	199.3
	85	0.25	2.5	325.0	311.6	200.1
	85	1	0.1	313.8	310.4	199.3
	85	1	0.2	320.9	311.7	200.1
	85	1	2.5	324.4	310.8	199.6
	85	2	0.2	316.2	306.7	196.9
	85	2	2.5	-	308.7	198.2
10.0	85	1	0.2	14.0	13.6	8.7
	85	1	2.5	-	14.0	9.0
	85	2	0.2	12.8	12.4	8.0
Solution set aside overnight before filtration -						
10.0	850	2	0.2	-	15.4	9.9
50.0	850	2	0.2	-	77.4	49.7
	1700	2	0.2	-	77.1	49.5
200.0	850	1	0.2	325.5	311.3	199.9
	1700	1	0.2	326.1	311.6	200.1
	850	2	0.2	324.7	310.2	199.2

(vi). The effect of different conditions on the determination of tungstophosphate with tri-n-butylamine

The method prescribed and modifications thereof were applied to portions of standard tungstate solution in order to ascertain the extent to which various factors could be altered without adverse effect on the recovery of tungsten. Phosphate in excess of 85 mg was added, as orthophosphoric acid, to acidified solutions. The results are shown in Table IV, in which all figures have been slightly modified to correspond to exactly 200, 50 or 10 mg of tungsten.

Except at low acidity, recovery of 10 mg of tungsten was not quantitative from solutions that had been set aside for only 1 hour before filtration, even if a large excess of precipitant had been added. For 200 mg of tungsten in presence of 85 mg of phosphate, the maximum permissible acidity was 1N. Precipitates set aside overnight before filtration gave acceptable results for 10 to 200 mg of tungsten in up to about 2N acid, even in presence of much more phosphate. An increase in the amount of tri-n-butylamine had comparatively little influence on recovery of tungsten, but contamination of precipitates was increased. Heating at 210°C reduced all weights to an acceptable level. Greater initial contamination of precipitates also occurred at higher acidities. In general, when larger amounts of phosphate were present and acidity was high, precipitates containing large or small amounts of tungsten required to be set aside overnight before filtration. The amount of tri-n-butylamine suitable for precipitation of 10 to 200 mg of tungsten in 100 ml of solution was 0.2 g.

TABLE V

EFFECT OF VARIOUS ACIDS AND SODIUM SALTS ON DETERMINATION OF TUNGSTOPHOSPHATE

Solutions were set aside for 18 hours before filtration

Amount of tungsten taken, mg	Amount of phosphate used, as PO_4, mg	Amount of acid present N	Amount of sodium salt present, g	Amount of tungsten found		
				sulphuric acid mg	nitric acid mg	hydrochloric acid, mg
10.0	85	0.25	-	9.9	10.0*	9.9*
	850	1	-	9.9	9.8	-
200.0	85	0.25	-	197.6*	200.3*	199.9*
	85	1	-	199.8	-	200.1*
	850	1	-	199.6	200.4	199.9
	850	1	5	199.6	200.0	199.8

* Filtration after 1 hour

(vii). The effect of other acids and sodium salts on the determination of tungstophosphate with tri-n-butylamine

The results of experiments in nitric or sulphuric acid, precipitant and wash solution being prepared in the same acid, are shown in Table V. The influence of sodium salts is also shown, and a few results from Table IV have been inserted to assist comparison. Sulphuric acid had a slight hindering effect on precipitation, and precipitates had to be set aside overnight for satisfactory recovery of tungsten. Nitric acid exerted no hindering effect, but the precipitates from 200 mg of tungsten had a brownish colour, which was associated with a small positive error.

Less than 0.1 mg of tungsten was detected in filtrates. Sodium salts had no significant effect.

Large amounts of perchloric acid could not be used because it formed a precipitate with the amine. With 200 mg of tungsten in 0.2N perchloric acid and addition of amine hydrochloride, the error in the weight of precipitate obtained after the solution had been set aside for 1 hour before filtration was +0.9 mg. The addition of 160 mg of sodium fluoride had apparently little effect, 199.6 mg of tungsten being found in the precipitate and 0.3 mg in the filtrate. When this experiment was repeated in a polythene beaker, 185.5 mg of tungsten were found in the precipitate and approximately 4 mg in the filtrate. Fluoride thus had an adverse effect, but small amounts would normally be removed by the glassware used. No silicon was found in the first precipitate as a result of the attack on glass.

3. Formation of Tungstophosphoric Acid from Metallic Tungsten and the Subsequent Precipitation by Tri-n-butylamine

(i) Direct dissolution of tungsten with acids

The addition of phosphoric acid to other mineral acids in the disintegration of tungsten-containing materials is a recognised method of obtaining solution and avoiding precipitation of tungstic acid (26). It is usually tacitly assumed that 12-tungstophosphoric acid is formed (see, however, p. 4). In the present work such a method appeared very suitable as the tungstophosphoric acid could thereafter be precipitated by tri-n-butylamine under conditions which have already been shown to be satisfactory.

To avoid complicating factors due to other elements, a tungsten powder of purity not less than 99.9% was first used. Disintegration with hydrofluoric and nitric acids, a mixture particularly effective with tungsten-containing materials, in the presence or with subsequent addition, of phosphoric acid, was favoured. Moreover, silica would be conveniently removed as silicon tetrafluoride. Use of aqua regia in the presence of phosphoric acid was also examined since aqua regia is another common acid mixture for materials containing tungsten.

Procedure A: Use of hydrofluoric, nitric and phosphoric acids.

To 200 mg of tungsten in a polytetrafluoroethylene beaker were added 0.58 ml of orthophosphoric acid (sp.gr. 1.75), 20 drops of 40% hydrofluoric acid and nitric acid drop by drop. After reaction had ceased, evaporation on a hot-plate at 200°C with an aircurrent impinging on the surface of the liquid converted the mixture into a syrupy mass. The latter was dissolved

TABLE VI

DETERMINATION OF TUNGSTEN AFTER DIRECT DISSOLUTION WITH ACIDS

	Experiment No.	Tungsten by tributyl-amine %	Tungsten in filtrate %	Total apparent recovery %
Procedure A	1	100.4	~ 0.1	100.5
	2	99.0	~ 0.5	99.5
	3 *	99.3	~ 0.8	100.1
Procedure B	4	99.9	~ 0.4	100.3
	5	100.1	~ 0.4	100.5

* Phosphoric acid was added after the dissolution with hydrofluoric and nitric acids.

in water and the solution transferred to a 250 ml glass beaker and made up to 100 ml, N in hydrochloric acid. Precipitation with tri-n-butylamine was effected as previously described (p. 20).

Procedure B: Use of aqua regia and phosphoric acid.

This method might not always be applicable because most tungsten materials contain at least some silicon which, if not removed, results in formation of the more stable tetrabasic 12-tungstosilicic acid (27).

To 200 mg of tungsten were added 0.58 ml of orthophosphoric acid, 10 ml of 12N hydrochloric acid and 2 ml of 16N nitric acid. 0.58 ml of phosphoric acid is approximately a 100-fold excess over the theoretical requirement for formation of 12-tungstophosphoric acid from 200 mg of tungsten. After tungsten had been dissolved by heating, the solution was diluted to 100 ml and assumed to be approximately N in hydrochloric acid. Precipitation with tri-n-butylamine was effected as before.

The results obtained for both procedures are given in Table VI.

While the main product of the disintegration appeared to be 12-tungstophosphoric acid, total recoveries tended to be slightly high and there were appreciable losses of tungsten to the filtrates. Results by Procedure A were erratic but unaffected by adding the phosphoric acid either before or after the dissolution. Procedure B gave more consistent results.

A probable cause of recoveries greater than 100% was thought to be the formation of small amounts of heteropoly acids with ratios of tungsten to phosphorus less than 12. Several such acids are known to exist (28), e.g., 11 and 9, which have basicities of 7 and 3, respectively, and could give rise to complexes of greater weight with tri-n-butylamine.

Next to 12-tungstophosphoric acid, 18-tungsto-2-phosphoric acid, $H_6P_2W_{18}O_{62}$, is the most common and stable. A sample of this acid (luteophosphotungstic acid) was prepared according to the method of Kehrmann (22). The tungsten content of an aliquot of a solution of the hydrated material was determined by degrading the heteropoly acid to tungstate with alkali, forming the 12-tungstophosphoric acid by acidifying in the presence of additional phosphate and precipitating with tri-n-butylamine. About 200 mg of tungsten as 18-tungsto-2-phosphoric acid were precipitated from 0.25N hydrochloric acid solution containing 850 mg of phosphate and the precipitate dried at 210°C under conditions shown to be satisfactory for the tri-n-butylamine complex of 12-tungstophosphoric acid. The weight of precipitate obtained was about 6% greater than that for the same amount of tungsten as 12-tungstophosphoric acid and corresponded to within 0.5% to that required for $[(C_4H_9)_3N.H]_6P_2W_{18}O_{62}$. Less than 0.1 mg of tungsten was found in the filtrate.

Hence, although the presence of some 18-tungsto-2-phosphoric acid might account for apparent high total recovery of tungsten it could not be responsible for the significant losses of tungsten to the filtrate in experiments 2 to 5. These might be caused by degradation of 12-tungstophosphoric acid. Even if 100% formation of the latter had occurred, extensive heating with phosphoric acid for removal of hydrofluoric acid, as in experiments 1 to 3, and heating with concentrated hydrochloric acid as in experiments 4 and 5 might result in at least some degradation analogous to that of the less stable 12-molybdophosphoric acid (27). Such degradation would only be reversed by raising the pH above 9 and reacidifying (29).

The more erratic results obtained by Procedure A might be associated with dehydration of orthophosphoric acid and formation of pyro- and polyphosphoric acids which do not revert to orthophosphoric acid except by mineral acid hydrolysis (30). Procedure B would not lead to formation of condensed phosphoric acids.

(ii). Alkali treatment after dissolution of tungsten with acids

In order to try to improve on the results of experiments 1 to 5, the effect of making the acid solution of the disintegrated material alkaline, and thus breaking down all complex tungstic acids, and then reacidifying the alkaline solution, as in the preliminary experiments with tungstate and phosphate, was investigated.

Procedure C: Use of sodium hydroxide.

Dissolution was carried out as in Procedure A. After the evaporation of the volatile acids the solution was made up to about 50 ml in a glass beaker and sodium hydroxide solution added until the pH was as shown in Table VII. The solution was stirred for 5 minutes then reacidified with 6N hydrochloric acid and tungstophosphate precipitated with tri-n-butylamine.

Procedure D: Sodium carbonate fusion.

Here, disintegration was effected in a platinum crucible with hydrofluoric and nitric acids in the absence of phosphoric acid. After dissolution was complete the solution was evaporated to dryness, and the separated tungstic oxide fused with 0.5 g of sodium carbonate. The melt was extracted with water, the solution reacidified with 6N hydrochloric acid in the presence of 85 mg of phosphate and precipitation carried out.

TABLE VII

DETERMINATION OF TUNGSTEN USING AN ALKALI TREATMENT AFTER DISSOLUTION WITH ACIDS

	Experiment No.	pH after addition of sodium hydroxide	Tungsten by tributyl-amine %	Tungsten in filtrate %	Total apparent recovery %
Procedure C	6	9.6	99.3	~0.4	99.7
	7	10*	99.6	~0.2	99.8
	8	>10	100.0	~0.2	100.2
Procedure D	9		99.7	~0.1	99.8
	10		99.6	~0.2	99.8
	11		99.5	~0.1	99.6

* Left overnight after addition of sodium hydroxide.

Since, in practice, evaporation with sulphuric acid would be required before sodium carbonate fusion in order to break down fluorides of metals originally associated with tungsten, this was carried out in experiment 11. Results are given in Table VII.

Where an alkali treatment was performed after the initial disintegration, total recoveries of tungsten were no longer consistently high and losses to the filtrates were in general reduced. Procedure D gave more consistent results. The somewhat lower result for experiment 11 was not considered to be significant as slight spattering occurred in fuming off sulphuric acid. In Procedure C, the necessity for making strongly alkaline, beyond pH 9.6, where 12-tungstophosphoric acid would be completely degraded (29), is evident. Since freshly formed tungstic acid is readily dissolved in sodium hydroxide solution, further improvement on the results of Procedure C might be made by substituting sulphuric acid for phosphoric acid in the initial acid treatment and adding a small amount of phosphate afterwards to the alkaline solution.

It thus seems that formation of 12-tungstophosphoric acid is more certain where alkaline solutions containing tungstate and phosphate are acidified. Before selecting a particular procedure, the influence of other elements was examined.

TABLE VIII

EFFECT OF VARIOUS ELEMENTS ON DETERMINATION OF 200.0 MG OF TUNGSTEN

Element	Amount of element added, mg	Amount of tungsten found by - Method I* mg	Amount of tungsten found by - Method II† mg	Amount of tungsten found in filtrate after - Method I* mg	Amount of tungsten found in filtrate after - Method II† mg
Calcium	700	200.4	199.8	~0.2	~0.8
Chromium^{III}	700	187.1	193.7	>6	>3
	100	198.3	-	~1.5	-
	25	198.6	-	~0.2	-
Cobalt^{II}	700	200.4	200.6	~0.3	~0.2
Copper^{II}	700	200.2	201.2	~0.6	< 0.1
Lead (HNO_3)	700	200.7	197.6	n.d.	n.d.
Manganese^{II}	700	200.3	199.9	< 0.2	~0.1
Nickel	700	200.0	200.2	< 0.2	< 0.2

* Precipitation from N hydrochloric acid; set aside overnight before filtration.

† Precipitation from 0.25 N hydrochloric acid; filtration after 1 hour.

4. The Influence of Various Elements on the Determination of Tungsten as Tris(tri-n-butylammonium) 12-Tungstophosphate

A study of the influence of some of the elements commonly occurring along with tungsten was made. It was assumed that if tungsten-containing compounds were dissolved directly in acid solutions (Procedures A and B, p. 25) addition of salts of the metals to acidified solutions of tungstophosphate would suffice. If, however, it was essential to make acid solutions alkaline, and then again acid (Procedures C and D, p. 29), it would be necessary also to examine the effects of other elements when they were present before solutions were made alkaline. Two sets of experiments were therefore done.

(i). Addition of salts to acidified solutions of tungstophosphate

Metallic chlorides were added to acidified solutions prepared from 200 mg of tungsten as tungstate and 850 mg of phosphate. Under the conditions of Procedures A and B (p. 25), this large amount of phosphate would be present. Lead was added as lead nitrate and nitric acid used. Precipitation with tri-n-butylamine was effected. Results are given in Table VIII.

Despite the large amounts of the various elements tested, only chromium caused serious error; somewhat smaller amounts would probably have been without influence. Chromium hindered precipitation of tungsten and, when a large amount was present, grossly contaminated the precipitate, which was yellow in colour. To a much lesser extent, copper and cobalt probably exerted comparable effects.

Of other elements examined, molybdenum as molybdophosphate formed

precipitates with the amine under the various conditions used for tungstophosphate. Alone, vanadium as vanadophosphate did not react, but, in conjunction with tungstate, it formed orange precipitates, presumably of tri-n-butylammonium tungstovanadatophosphate. Precipitates formed in presence of iron$^{II \text{ and } III}$ were heavily charred at 210°C and were up to 15% heavy. As iron is a constituent of virtually all tungsten materials, this effect was studied in detail at a later stage.

(ii). Addition of salts to solutions of tungstophosphate that were afterwards made alkaline and then acid

Chlorides of the metals were added to solutions containing 200 mg of tungsten as tungstate and 43 mg of phosphate, of which a large excess would not be required under the suggested revised conditions of formation of tungstophosphoric acid by Procedure C (p. 31). 3 Ml of 12N sodium hydroxide solution were added to the stirred solutions which were heated to about 80°C. The mixtures were rapidly acidified with hydrochloric acid (nitric for lead) and made up to 100 ml N in acid.

As shown in Table IX some additional elements were included in the tests. Tantalum and niobium fluorides were added to tungsten powder which was digested with hydrofluoric, sulphuric and nitric acids, extracted with sodium hydroxide solution and acidified in the presence of phosphate as usual. When the mixture had a volume of 40 ml and was N in hydrochloric acid, a white precipitate which had formed was filtered off in a glass filtering crucible, and the filtrate prepared as above.

Precipitation with tri-n-butylamine was effected in all solutions

TABLE IX

EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF 200.0 MG OF TUNGSTEN

Element	Weight of element mg	Recovery of tungsten %	Tungsten in filtrate %
Aluminium	100	98.5	~1.2
Calcium	200	99.8	~0.7
*	200	100.5	< 0.1
*	50	99.9	< 0.4
$Cobalt^{II}$ †	200	100.4	0
$Copper^{II}$	200	100.6	0
Lead (HNO_3)	200	100.2	n.d.
$Manganese^{II}$	200	102.3	~0.2
†	200	100.1	< 0.1
Nickel	200	100.2	< 0.1
Tin^{IV}	25	100.6	~0.3
Titanium	10	105.8	~1.5
Tantalum	5	104.8	~0.4
plus niobium	5		

* In presence of excess sulphate.

† Ascorbic acid (100 mg) added before precipitation.

and results obtained are shown in Table IX.

Prior to addition of tri-n-butylamine manganese solutions were pink, presumably due to manganese^{III} (31), which interfered with the determination of tungsten. 100 Mg of ascorbic acid, added before precipitation, successfully eliminated the interference. As the reacidified solution containing cobalt was brownish-pink, ascorbic acid was also added to it before precipitation of the tungstophosphate.

It is evident that considerable amounts of calcium, cobalt, copper, lead, manganese and nickel may be present with tungsten under the prevailing conditions, but only a moderate amount of aluminium and a small amount of tin are permissible. Even very small amounts of titanium, tantalum and niobium will have an adverse effect. Iron, chromium, molybdenum and vanadium, the nature of whose interference has already been indicated (pp. 33 , 34), would still be expected to interfere seriously. As the interference of iron was rather unusual and iron is likely to be present in most tungsten-containing materials it was decided to examine its behaviour more thoroughly. For convenience, data relating to the earlier experiments are included in the following section.

TABLE X

EFFECT OF IRON SALTS ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRI-n-BUTYLAMINE

Iron added mg	Precipitate obtained at 140°C mg	Ignition product at 750°C mg	Ratio of weights obtained at 140° and at 750° R_{140}	Iron in ignition product mg	Phosphorus in ignition product mg	Tungsten in filtrate mg
$Iron^{II}$						
25	337	263	1.28	2.4	2.6	~ 0.5
150	347	266	1.31	3.9	3.4	~ 0.5
700	357	267	1.33	4.9	4.1	~ 0.5
1400	356	267	1.33	5.6	3.2	~ 0.5
$Iron^{III}$						
25	355	267	1.33	5.1	3.2	~ 0.5
280	354	266	1.33	-	-	-
1400	352	264	1.33	5.9	2.9	~ 4

5. Detailed Study of the Behaviour of Iron during Precipitation of Tungstophosphate with Tri-n-butylamine

(i). Addition of iron salts to acidified solutions of tungstophosphate

Solutions of sodium tungstate equivalent to 200 mg of tungsten and containing disodium hydrogen phosphate equivalent to 85 mg of phosphate (PO_4) were gradually acidified with hydrochloric acid, iron^{II} or ^{III} sulphate was added and precipitation carried out as before, except that 50% more tri-n-butylamine was used. The onset of precipitation was usually retarded in the hot solutions until about 20% of the reagent solution had been added. Unless otherwise indicated, precipitates were left overnight before filtration, then separated and dried at 140°C. Thereafter the precipitates were transferred in known amounts to platinum crucibles for ignition at 750°C, and then the iron and phosphorus contents were determined (Appendix pp.97, 96). Results are given in Table X.

As the amount of iron^{II} increased, the weight of the precipitate obtained after drying at 140°C increased to a maximum. A much smaller amount of iron^{III} gave a similar result. In an additional experiment even 1 mg of iron^{III} was found to increase the precipitate weight by several milligrams. Ignition products of the heaviest precipitates appeared to correspond to $Fe_2O_3.P_2O_5.24WO_3$ (200 mg of tungsten = 265.9 mg, containing 5.1 mg of iron and 2.8 mg of phosphorus). This suggested that the amine had coordinated about the iron^{III} ion in the original precipitates - cf. Jean's inorganic amine complexes, e.g., $[P(W_2O_7)_6H_4][Co(NH_2CH_2CH_2NH_2)_2(SCN)_2]_3.16H_2O$ (19).

A 71-mg portion of the precipitate obtained in the experiment made with 280 mg of iron^{III} was heated in a Stanton recording thermobalance and

VARIATION IN WEIGHT PER 100 mg OF PRECIPITATE

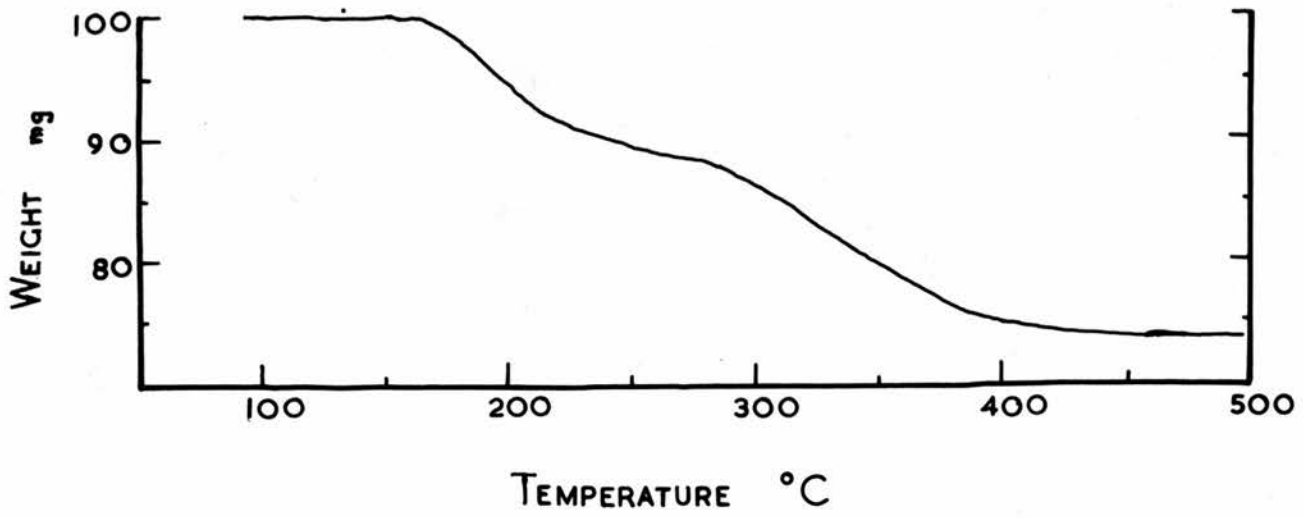

Figure 3.

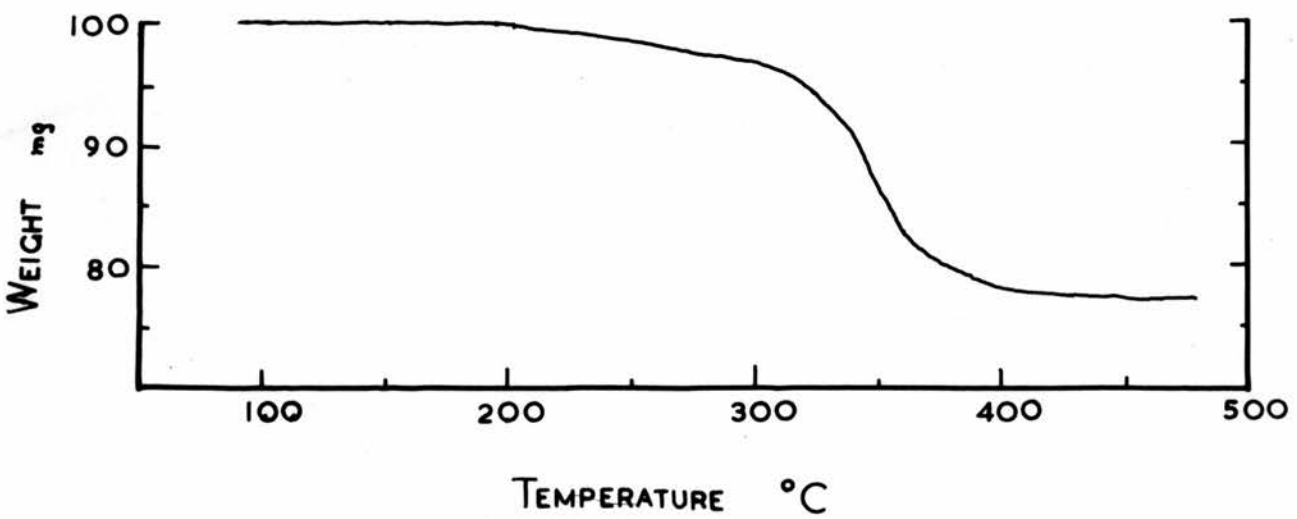

Figure 4.

the results are shown in Fig. 3. It is notable that the temperature found suitable for the tris(tri-n-butylammonium) 12-tungstophosphate, viz., 210°C, where excess reagent has been volatilised, was useless for the iron-containing complex, which underwent decomposition before this temperature was reached. A temperature between 100 and 150°C was necessary and 140°C was selected for further use. Iron-containing precipitates heated to 210°C charred heavily. This later proved useful in indicating where tris(tri-n-butylammonium) 12-tungstophosphate precipitates were contaminated with iron.

The determination of carbon, hydrogen and nitrogen (Appendix p. 98) in further portions of the desiccator-dried precipitate, suggested that the dihydrate of aquopentakis(tri-n-butylamine)iron^{III} 12-tungstophosphate was formed. (Found: C, 18.3; H, 3.57; N, 1.75. $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}.2H_2O$ requires C, 18.4; H, 3.63; N, 1.79%). 0.1% of water was absorbed on exposure of the precipitate to an atmosphere of 50% relative humidity.

The use of a very large excess of the amine increased the weight of the precipitate by only 1 mg.

Although 12-tungstophosphoric acid that had been degraded by means of an excess of sodium hydroxide solution and then reformed in presence of additional phosphate by slow or rapid addition of acid, gave with tri-n-butylamine the weight of precipitate expected for undegraded material, it was now found that rapidly acidified solutions of degraded tungstophosphoric acid, to which ferric chloride and tri-n-butylamine were then added, gave variable lower weights of precipitates and values of R_{140} than slowly acidified solutions, which alone gave the same results as undegraded heteropoly acid to which hydrochloric acid and ferric chloride were added. All tabulated

TABLE XI

ANALYSIS OF A TUNGSTOPHOSPHATE PRECIPITATE (W = 200.0 MG) CONTAINING IRON AND CINCHONINE

Composition of material	Weight of precipitate 105°C mg	Weight of precipitate 750°C mg	Carbon %	Hydrogen %	Nitrogen %
Unknown	342.9	266.1	15.6	1.58	1.92
Calculated for $\left[Fe_2(H_2O)_2(C_{19}H_{22}ON_2)_5\right]\left[PW_{12}O_{40}\right]_2$	334.1	265.9	15.5	1.56	1.90
As above + $8H_2O$	340.6	265.9	15.2	1.74	1.86
As above + $8H_2O$ + 0.18 mole of additional cinchonine	343.2	265.9	15.6	1.78	1.92

results relate to gradually acidified solutions.

The same general effects were observed when 2:4-dimethylquinoline, 8-hydroxyquinoline or cinchonine replaced tri-n-butylamine. With cinchonine, 200 mg of tungsten yielded 342.9 mg of precipitate heated at 105°C and 265.9 mg heated at 750°C. A 166-mg portion of the precipitate was heated in a Stanton recording thermobalance and the results are shown in Fig.4. The behaviour of the iron-containing cinchonine precipitate differed little from that of the simpler cinchonine precipitate, weight being constant from 100 to 200°C, but loss of weight above 200°C was more rapid.

Analyses of further portions of the precipitate for carbon, hydrogen and nitrogen were made. As the desiccator-dried precipitate rapidly absorbed about 3% of water on exposure to the atmosphere, it was allowed to reach equilibrium in an atmosphere of 50% relative humidity before portions were taken for weighing. In Table XI results relating to the original desiccator-dried precipitate are shown, together with results calculated for substances of various compositions.

If the percentage of hydrogen, which is the least reliable determination, is ignored, then it is seen that the composition corresponds closely to that required for $\left[Fe_2(H_2O)_2(C_{19}H_{22}ON_2)_5\right]\left[PW_{12}O_{40}\right]_2.8H_2O$ with, however, an additional 0.18 mole of cinchonine attached. There is thus marked resemblance to the compound, $\left[Fe(H_2O)(C_{12}H_{27}N)_5\right]PW_{12}O_{40}.2H_2O$, obtained with tri-n-butylamine in presence of iron.

It would therefore appear that where tungsten is determined by acid hydrolysis and addition of cinchonine, in solutions containing iron and a little phosphorus (as in steels), contamination of the precipitate with iron

TABLE XII PART I

EFFECT OF VARYING AMOUNTS OF PHOSPHATE ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRI-n-BUTYLAMINE IN PRESENCE OF IRON SALTS

200.0 Mg of W = 354.7 mg (Wt_{140}) of $[Fe(H_2O)(C_{12}H_{27}N)_5]PW_{12}O_{40}.2H_2O$ (heated at 140°) = 265.9 mg (Wt_{ign}) of $Fe_2O_3.P_2O_5.24WO_3$;
R_{140}, the ratio of these weights, is 1.334.

200.0 Mg of W = 311.5 mg (Wt_{210}) of $(C_{12}H_{27}N.H)_3PW_{12}O_{40}$ (heated at 210°) = 258.6 mg (Wt_{ign}) of $P_2O_5.24WO_3$;
R_{210}, the ratio of these weights is 1.204.

Hydrochloric acid N	Phosphate (PO_4), mg	Weight of iron^{III} present, mg											
		25			100			280			700		
		Wt_{140}	Wt_{ign}	R_{140}	Wt_{140}	Wt_{ign}	R_{140}	Wt_{140}	Wt_{ign}	R_{140}	Wt_{140}	Wt_{ign}	R_{140}
0.2	85	354.1*	267	1.33	-	-	-	353.7*	265	1.33	349.3*	262	1.34
	425	356.2†	266	1.34	355.0†	264	1.34	349.4†	260	1.34	341.9†	255	1.34
		-	-	-	355.0	265	1.34	-	-	-	-	-	-
	850	-	-	-	341.6	257	1.33	-	-	-	331.3	248	1.34
0.5	85	-	-	-	-	-	-	-	-	-	354.6†	265	1.34
	425	345.8†	264	1.31	354.3†	265	1.34	354.2†	265	1.34	349.6	261	1.34
	850	352.9	266	1.33	352.7	264	1.34	352.2†	263	1.34	346.3	259	1.34
1.0	425	-	-	-	-	-	-	-	-	-	352.3†	264	1.33
	850	337.0	263	1.28	329.8	260	1.27	346.9	263	1.32	341.9	258	1.33
	1700	-	-	-	-	-	-	330.4	251	1.31	331.0	251	1.32
2.0	850	-	-	-	326.9	259	1.26	328.9	259	1.26	328.4	258	1.27
	1700	-	-	-	-	-	-	-	-	-	327.6	261	1.26

* Filtration after 1 hour. † 12-Tungstophosphoric acid was used.

may be due to its becoming a constituent of the precipitate and **not** merely to its being coprecipitated (32).

In further experiments with tri-n-butylamine the amounts of acid and phosphate were varied. Either a standard solution was prepared by gradually acidifying a solution containing sodium tungstate and a 10-fold excess of disodium hydrogen phosphate, or a solution of 12-tungstophosphoric acid was standardised by precipitation with tri-n-butylamine. Additional phosphate, as orthophosphoric acid, and iron salts were added to acidified solutions, the volumes of which were made up to 100 ml for precipitation with tri-n-butylamine.

It rapidly became apparent that the nature of the precipitate depended to a considerable extent on the conditions. Thus, the precipitate weight at 140°C tended to decrease with increasing acidity of the original solution. This could be due to formation of the iron-free complex or to incomplete precipitation of tungsten. The complex was therefore ignited at 750°C and the ratio of the weight of the complex to that of the ignition product, R_{140}, calculated as a means of discriminating between the two effects. The results obtained are shown in Table XII Part I.

Under no conditions was a precipitate obtained with a value of R_{140} significantly greater than that corresponding to $\left[Fe(H_2O)(C_{12}H_{27}N)_5\right]PW_{12}O_{40}.2H_2O$. With high concentrations of phosphate and also high concentrations of iron at not too high acidity, weights tended to be low due to incomplete precipitation; the value of R_{140} remained essentially constant showing that the composition of the precipitate had not altered. With increasing acidity the composition altered towards that of the iron-free tri-n-butylamine complex.

TABLE XII PART II

EFFECT OF VARYING AMOUNTS OF PHOSPHATE ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRI-n-BUTYLAMINE IN PRESENCE OF IRON SALTS

See heading for Part I

Hydrochloric acid N	Phosphate (PO_4), mg	Weight of iron^{III} present, mg											
		25			100			280			700		
		Wt_{210}	Wt_{ign}	R_{210}	Wt_{210}	Wt_{ign}	R_{210}	Wt_{210}	Wt_{ign}	R_{210}	Wt_{210}	Wt_{ign}	R_{210}
1.0	850	320.4	263	1.22	-	-	-	-	-	-	-	-	-
	1700	-	-	-	-	-	-	314.5	251	1.25	316.1	251	1.26
2.0	850	-	-	-	312.4	259	1.20	-	-	-	-	-	-
	1700	-	-	-	-	-	-	-	-	-	312.7	261	1.20
		Weight of iron^{II} present, mg											
					100						700		
2.0	850				311.6	260	1.20				311.9	260	1.20

If solutions contained 85 mg of phosphate and 0.2to say 0.5N hydrochloric acid, conditions could perhaps be arranged for the determination of tungsten in presence of 25 to 700 mg of iron, although this was not examined rigorously. With 425 mg of phosphate and 0.2 or 0.5N acid, the amount of iron permissible would be limited and, with 850 mg of more phosphate, no conditions appeared satisfactory for the determination of tungsten as the iron-containing complex. It was thus apparent that only under very restricted conditions might 12-tungstophosphate be determined in presence of iron as the aquopentakis(tri-n-butylamine)iron^{III} complex.

For 2.0N hydrochloric acid solutions, the values of Wt_{ign} approached these required for tris(tri-n-butylammonium) 12-tungstophosphate. The high values for Wt_{140} indicated that the precipitates were probably contaminated by excess reagent which is only satisfactorily removed at 210°C. Weights of precipitate at 210°C were therefore recorded for some of the above experiments and are given in Part II of Table XII along with some results obtained when iron^{II} was substituted for iron^{III}. The effect of iron^{II} was examined since results in Table X had already shown that it had less influence on the precipitation. A solution was prepared by dissolving spongy iron in hydrochloric acid in an atmosphere of carbon dioxide.

In the experiments relating to 2.0N hydrochloric acid solutions, results are close to those required for $(C_{12}H_{27}N.H)_3PW_{12}O_{40}$, particularly where iron^{II} was used. Ignition products contained 0.4 and 0.9 mg of iron when 100 and 700 mg of iron^{III}, respectively, were present during precipitation, but less than 70μg of iron when iron^{II} was used. Thus by using 2.0N or higher hydrochloric acid concentration, formation of the tris(tri-n-butylammonium) complex is almost completely attained in solutions containing

iron^{II} and may possibly be attained in solutions containing less than 100 mg of iron^{III}.

(ii). Attempts to eliminate the interference of iron^{III}

For disintegration of tungsten-containing materials and formation of tungstophosphoric acid in acid solutions, a large amount of phosphate must be present to prevent precipitation of tungstic acid. The maximum weight of phosphate tolerable for determination of tungsten as the aquopentakis (tri-n-butylamine)iron^{III} complex is 425 mg. Although this was considered to be insufficient for holding 200 mg of tungsten in solution, an attempt was made to utilise this approach.

200 Mg of tungsten were dissolved in hydrofluoric and nitric acids according to Procedure A (p. 25) but in presence of only 0.3 ml of phosphoric acid (425 mg of phosphate). Due to the small amount of phosphate, partial separation of tungstic acid occurred during evaporation and difficulty was encountered in obtaining solution. However, the solution was eventually made up to 100 ml, 0.5N in hydrochloric acid, and 100 mg of iron^{III} were added. Attempted precipitation as the aquopentakis(tri-n-butylamine)iron^{III} complex gave a recovery of 97.7% of tungsten, R_{140}, 1.33 and 3 mg of tungsten in the filtrate.

If, in a material containing iron, 12-tungstophosphoric acid were formed in presence of iron by making the solution alkaline and then again acid, as would be required in Procedure C (p. 29), a large concentration of phosphate would not be essential, since precipitated tungstic acid readily dissolves in sodium hydroxide solution, but evaporation with

sulphuric acid, before addition of alkali, would be necessary for complete elimination of fluoride. Presence of only a small amount of phosphate, viz. 85 mg, extends the range of conditions under which the aquopentakis (tri-n-butylamine)iron^{III} complex is quantitatively formed.

To test this, 200 mg of tungsten as sodium tungstate and 85 mg of phosphate as the disodium salt, were dissolved in water, 50 mg of iron^{III} as ferric chloride were added and the solution was made alkaline with 1 ml of 6N sodium hydroxide solution. 6N hydrochloric acid was added slowly until pH 2 was reached and then 4 ml in excess. The solution was made up to 100 ml and was 0.25N in hydrochloric acid. Precipitation with tri-n-butylamine was effected. Recovery of tungsten as the aquopentakis(tri-n-butylamine)iron^{III} complex was low by several per cent and again a loss of 3 mg of tungsten to the filtrate occurred.

Precipitation of the aquopentakis(tri-n-butylamine)iron^{III} 12-tungstophosphate was thus not only restricted to a narrow range of conditions but also could not readily be applied to iron-containing tungsten materials such as ferrotungsten.

Application of high acid concentration to suppress interference of iron, in the determination of tungsten as tris(tri-n-butylammonium) tungstophosphate was tried in the analysis of a ferrotungsten containing about 20% of iron. 200 Mg of tungsten as ferrotungsten were dissolved in hydrofluoric, nitric and phosphoric acids as in Procedure A (p. 25). The solution after removal of the volatile acids contained 50 mg of iron^{III} and 850 mg of phosphate and was made up to 2N in hydrochloric acid. Tungsten found as the tris(tri-n-butylammonium) complex was 80.6% for 81.3% but more

than 1 mg of iron was present in the precipitate and 3 mg of tungsten were in the filtrate, which did not accord with the nearest comparable result given in Part II of Table XII.

Thus, attempts to determine tungsten in the presence of $iron^{III}$, either as aquopentakis(tri-n-butylamine)$iron^{III}$ 12-tungstophosphate, or as tris(tri-n-butylammonium) 12-tungstophosphate, were unsuccessful.

(iii). The elimination of the interference of $iron^{III}$ by reduction to $iron^{II}$

Since considerable amounts of $iron^{II}$ could be tolerated in the precipitation of tris(tri-n-butylammonium) 12-tungstophosphate in 2N hydrochloric acid solution (Table XII Part II), methods of reducing $iron^{III}$ in presence of 12-tungstophosphate were examined. The reduction of 100 mg or more of $iron^{III}$ in a small volume of solution, however, is not readily attained.

The addition of a reductant to the solution was considered to be the most convenient method. As stannous chloride and zinc both reduce tungstate and tungstophosphate, the use of sulphur dioxide was examined. 100 Ml of solution, 0.25N in hydrochloric acid, containing 300 mg of $iron^{III}$ as ferric chloride and 850 mg of phosphate, were saturated with sulphur dioxide and then boiled. Despite prolonged treatment, testing with ammonium thiocyanate showed that approximately 10 mg of $iron^{III}$ remained. The large amount of iron, the acidity or the phosphate present, presumably prevented complete reduction (33). This method was not further examined.

Use of the silver reductor

The silver reductor (34) which can be used for the reduction of $iron^{III}$

in N hydrochloric acid solution was tried and found not to reduce tungstophosphate excessively at this acid concentration. The size of the column used and the amount of silver had to be restricted in order to keep the volume of the reduced solution down, and only a limited amount of iron^{III}, probably not more than 100 mg could be dealt with. Preliminary experiments were made with acidified 12-tungstophosphoric acid solutions containing 850 mg of phosphate, to one of which 100 mg of iron^{III} as ferric chloride were added.

A column (length 14 cm, diameter 1 cm) containing 18 g of silver was employed. 50 Ml of sample solution, N in hydrochloric acid, and appropriate washings were passed through the reductor. The acid concentration of the blue effluent, which gradually lost its colour on heating in air, was raised to 2N before precipitation with tri-n-butylamine and separation of the precipitate as usual. 200 Mg of tungsten, alone and in presence of 100 mg of iron yielded 311.5 and 311.7 mg of precipitate respectively. About 0.4 mg of tungsten found in the filtrates was balanced by a little silver chloride in the precipitate.

A few experiments were made on the determination of tungsten in presence of iron, under conditions that might prevail in solutions obtained in accordance with Procedure C (p. 46).

(a). 100 Mg of iron^{III} were added to an alkaline solution containing 200 mg of tungsten^{VI} and 850 mg of phosphate, and acidification with hydrochloric acid was effected. After reduction, tri-n-butylamine was added to a 2N acid solution, and the precipitate separated and dried at 210°C. It weighed 320.4 mg and was heavily contaminated by iron. 0.4 Mg of tungsten

was found in the filtrate.

(b). The experiment was repeated but only with 43 mg of phosphate present. 310.2 Mg of iron-free precipitate were obtained but 2 mg of tungsten were recovered from the filtrate.

(c). The more successful reduction indicated by (b) was applied to ferro-tungsten. A sample containing 200 mg of tungsten and 50 mg of iron was disintegrated with hydrofluoric and nitric acids in presence of 1 ml of sulphuric acid which was added to ensure breakdown of ferric fluoride during evaporation to remove the volatile acids. The solution afterwards obtained was made strongly alkaline, 43 mg of phosphate were added and the hot solution was rapidly acidified with hydrochloric acid. The procedure for (b) was then followed. The precipitate obtained (318.6 mg) was heavily charred and contained iron but only 0.1 mg of tungsten was found in the filtrate.

Large amounts of phosphate and sulphate seemed to be exerting comparable adverse effects when solutions, containing both tungsten and iron, were made alkaline and then acid, before passage through the reductor. Some $iron^{III}$ seemed to become inaccessible to reduction. However, when the amount of phosphate was reduced and sulphuric acid excluded, the satisfactory nature of the precipitate was counterbalanced by loss of too much tungsten to the filtrate.

Use of ascorbic acid

The problem of satisfactorily determining tungsten with tri-n-butyl-amine in presence of even 50 to 100-mg amounts of iron remained unsolved where 12-tungstophosphoric acid had to be produced from tungsten-containing

TABLE XIII

REDUCTION OF IRON^{III} BY ASCORBIC ACID

200.0 Mg of W = 311.5 mg of $(C_{12}H_{27}N.H)_3PW_{12}O_{40}$

= 354.7 mg of $\left[Fe(H_2O)(C_{12}H_{27}N)_5\right]PW_{12}O_{40}.2H_2O$

5 Mg of iron^{III} = 8 mg of ascorbic acid

Hydrochloric acid present	Iron present	Ascorbic acid added	Weight of precipitate dried at 210°C
N	mg	mg	mg
1.0	0	100	312.0
1.0	2	100	311.6
1.0	5	8	317.2
1.0	5	50	315.5
1.0	25	40	324.8
1.0	25	150	316.7
0.25	2	40	312.1

materials. However, as determination of tungsten might frequently be required in materials containing only minor amounts of iron, some experiments were made to find if ascorbic acid, which is a recognised reductant for titrimetric determination of iron (35), might be an effective reducing agent.

Amounts of $iron^{III}$, as shown in Table XIII, were added to alkaline solutions containing 200 mg of $tungsten^{VI}$ and 85 mg of phosphate, which were then acidified. Before precipitation with tri-n-butylamine, ascorbic acid was added. After the solutions had been stirred for approximately 30 seconds the yellow colour disappeared, the solutions became faintly blue and tri-n-butylamine reagent was immediately added. Slight reduction of 12-tungstophosphate did not have an adverse effect.

In N hydrochloric acid 5 and 25 mg of $iron^{III}$ were not quantitatively reduced by the theoretical amounts of ascorbic acid, and large excesses of reductant gave only slight improvement. 2 Mg were satisfactorily reduced in 0.25 and 1N hydrochloric acid by a large excess of ascorbic acid.

Only small amounts of $iron^{III}$ could apparently be quantitatively reduced and in subsequent experiments 100 mg of ascorbic acid were added to N hydrochloric solutions for reduction of quantities of $iron^{III}$ up to 2 mg.

6. Adsorption of Tungstophosphoric Acid by Cellulose

Suppression of the interference of iron in situ, having been in general unsuccessful, methods of separation from tungsten were considered. Separation of much iron as the hydroxide, from alkaline solution of the tungstate, appeared unsuitable as some tungsten would likely be entrained by the gelatinous precipitate which would also be difficult to filter off. While various possibilities, such as use of cation exchange resins and solvent extraction were considered, a method which had suggested itself in an earlier part of this work was first examined.

In a number of tentative experiments on disintegration of ferrotungsten, very small residues were left after treatment with hydrofluoric, nitric and phosphoric acids (Procedure A). After hydrochloric acid had been added the residues were filtered off on filter paper and the latter washed with dilute hydrochloric acid. Deficiencies of tungsten that were obviously too large to be attributed entirely to the residue, were observed in these experiments. Ignition of the filter papers gave greenish residues of up to 10 mg which roughly corresponded to the missing tungsten. The effect was concluded to be adsorption of 12-tungstophosphoric acid by the cellulose. This was confirmed by passing the same 12-tungstophosphate solution through a series of filter papers, each of which, after washing, gave on ignition a residue that contained a similar weight of tungsten. No tungsten was lost when the solution was passed through a fine-pore sintered glass crucible. It therefore appeared that a column of cellulose might, by adsorption of 12-tungstophosphate, give a separation of tungsten from iron and many other elements.

TABLE XIV

PAPER-STRIP CHROMATOGRAPHY WITH TUNGSTOPHOSPHORIC ACID

	Developing solvent							
	10N Hydrochloric acid, N in phosphoric acid and 1.5 N in nitric acid		6N Hydrochloric acid		3N Hydrochloric acid		N Hydrochloric acid	
	R_f W	Fe	R_f W	Fe	R_f W	Fe	R_f W	Fe
12-tungstophosphoric acid	0		0		0		0	
18-tungsto-2-phosphoric acid	n.d.		0		n.d.		0	
12-tungstophosphoric acid and iron^{III}	n.d.		0	0.9	0 0.06	0.9	0 0.15	0.9
18-tungsto-2-phosphoric acid and iron^{III}	n.d.		n.d.		n.d.		0	0.9

(i). Paper-strip chromatography

A study was made of the behaviour of tungstophosphoric acid on paper strips to determine whether separation from iron was practicable. Although 12-tungstophosphoric acid is reputed to be formed on acidification of tungstate and phosphate in solution, it was of interest to examine the behaviour of another of the tungstophosphoric acids, of which 18-tungsto-2-phosphoric acid is the most common.

25-Microgram amounts of tungsten as 12-tungstophosphoric acid or as 18-tungsto-2-phosphoric acid were spotted on 1 cm paper strips. 25 Micrograms of iron as a 1% ferric chloride solution were applied on top of some of the air-dried tungstophosphate spots. Chromatograms were run for 2 to 3 hours with various developing solvents and, after drying, were sprayed with 0.5% 8-hydroxyquinoline in aqueous ethyl alcohol (6+4) and suspended over concentrated ammonia in a covered jar. Iron was shown as a black spot and tungsten usually appeared as a faint yellow spot. Spraying with concentrated hydrochloric acid turned the tungsten spot dark brown. The coloration faded slightly on standing and drying of the spraying reagents. The reaction for tungsten is based on the spot test suggested by Sousa (36). Results are given in Table XIV.

Both 12-tungstophosphoric and 18-tungsto-2-phosphoric acids, when alone, were quantitatively retained at the start in the original spots. It is apparent that phosphoric acid which was present when adsorption of tungstophosphoric acid by filter paper was first detected (p. 53), was not essential for adsorption, and that even N hydrochloric acid gave complete retention. With 6N hydrochloric acid 12-tungstophosphoric acid in

presence of iron^{III} was excellently separated from the latter which travelled almost at the solvent front. With low concentrations of hydrochloric acid, however, the 12-tungstophosphoric acid progressively split into a double band. This splitting of the heteropoly acid band was not observed with 18-tungsto-2-phosphoric acid and iron^{III} in N hydrochloric acid. When a chromatogram of 12-tungstophosphoric acid and iron^{III}, on which the iron had been removed to R_f 0.9 by means of 6N hydrochloric acid as solvent, was rerun on the same strip with N hydrochloric acid, a double band was again formed. It was therefore thought that the double band might be due to a tungstophosphate - iron interaction product which was not separated from the main heteropoly acid band when 6N hydrochloric acid was used as solvent. The amount of iron found with the tungsten would be very small. The behaviour of 12-molybdophosphoric acid was also examined under similar conditions. Molybdenum was likewise detected with oxine, giving a weak blue-green coloration. With 6N hydrochloric acid as solvent, molybdenum gave a continuous band from the start to R_f 0.6. With 3N and N hydrochloric acid progressively more molybdenum was retained at the start. This suggested that 12-molybdophosphate was continuously degrading particularly in acid solutions of higher concentration to a form which travelled on the paper. When a solution in 3N hydrochloric acid was boiled before it was spotted on the paper, the yellow coloration was removed from the solution and on developing a chromatogram with 6N hydrochloric acid all the molybdenum was obtained in a sharp band at R_f 0.62. When 12-tungstophosphoric acid was present, heating in 3N acid failed to remove the yellow coloration of 12-molybdophosphate, but in 6N acid the coloration was

slowly removed. By this means a separation of the two heteropoly acids was achieved on paper strip. It would appear that 12-molybdophosphate was degraded to molybenyl ions (27) while the more stable 12-tungstophosphate remained unaltered.

In hydrochloric acid of concentrations from 1 to 6N, iron was sufficiently separated from tungstophosphoric acid to merit application of the method on a larger scale, a column of cellulose being used in place of a paper strip. 6N hydrochloric acid was provisionally selected as the mobile phase as it had not only given the best separations of iron and 12-tungstophosphoric acid on paper strips, but was also potentially useful for degrading 12-molybdophosphoric acid.

(ii). Tentative experiments on the use of columns of cellulose

Columns of 1.5 cm glass tubing fitted with capillary stopcocks were used to contain 3.5-g quantities of cellulose powder added as a slurry either in water or in 6N hydrochloric acid. The flow-rate was initially 2 to 3 ml per minute but decreased with prolonged use due to closer packing of the cellulose.

In preliminary experiments, approximately 70-mg amounts of tungsten as 12-tungstophosphoric acid in 10 ml of 6N hydrochloric acid, containing 0.3 ml of 89% orthophosphoric acid, were applied to cellulose columns which had been equilibrated with 6N hydrochloric acid. 50 Mg of $iron^{III}$ or $chromium^{III}$ were also added in two experiments. Elution with 35 ml of 6N hydrochloric acid was sufficient to remove all iron from the column where this was originally present. This first fraction was henceforth

TABLE XV

QUANTITATIVE EXPERIMENTS ON SEPARATION OF 12-TUNGSTOPHOSPHORIC ACID FROM IRON^{III} AND CHROMIUM^{III}

Solution applied to column	Weight of tungsten in precipitate (210°), mg	Tungsten found in "iron fraction" mg	Tungsten found in filtrate, mg
Direct precipitation	67.3	-	~ 0.2
12-tungstophosphoric acid	66.2	~ 0.2	~ 1.1
12-tungstophosphoric acid and iron^{III}	66.0	~ 0.1	n.d.
12-tungstophosphoric acid and chromium^{III}	66.3	~ 0.1	n.d.

designated the "iron fraction", regardless of whether iron was present or not. 10 Ml of water, 30 ml of 0.2N sodium hydroxide solution and 30 ml of water were successively added to elute tungsten. 0.6 Ml of orthophosphoric acid was added to this fraction which was then made up to 100 ml approximately 0.5N in hydrochloric acid before precipitation with tri-n-butylamine. A comparison was made with an aliquot of the same 12-tungstophosphoric acid solution which was directly treated with tri-n-butylamine under the same conditions. Results are given in Table XV.

Recoveries of tungsten as tris(tri-n-butylammonium) 12-tungstophosphate were all approximately 98% of the result obtained by direct precipitation and the precipitates were obviously free from iron and chromium. 0.2 Mg or less of tungsten was found in the "iron fraction", a portion of which had been tested with dithiol (Appendix p. 95), and further elution of the cellulose column yielded none. When the filtrate from the precipitation with tri-n-butylamine in the second experiment was examined, an amount of tungsten corresponding to the deficiency was detected.

Retention of 12-tungstophosphoric acid by the cellulose and separation from iron and chromium were therefore satisfactory. It was concluded that during elution from the column, part of the 12-tungstophosphate had been degraded to tungstate with sodium hydroxide and subsequent reacidification in the absence of excess phosphate had failed to yield 12-tungstophosphoric acid quantitatively. In further work this difficulty was overcome, either by eluting with sodium hydroxide solutions containing phosphate, or by degrading and reforming all the tungstophosphate in presence of excess phosphate.

TABLE XVI

DETAILED STUDY OF THE ADSORPTION BEHAVIOUR OF AUTHENTIC 12-TUNGSTOPHOSPHORIC ACID

Composition of applied solution of hydrochloric acid	Tungsten in 50 ml effluent fractions, mg		
6N	0.1	0.01	0
6N, boiled 20 minutes and cooled	1.1	0.3 (25 ml)	
6N, 0.3M in phosphoric acid*	0.15	0.01	
6N, 0.3M in phosphoric acid,* boiled 20 minutes and cooled	3.5	0.02	
2N	0.15	0.08	
2N, boiled 20 minutes and cooled	<0.2	0	0.15
N, 0.5M in phosphoric acid*	1.5 (65 ml)		
0.5N	60	70	
6N, containing 200 mg of iron^{III}	0.3	0	0
6N, 0.3M in phosphoric acid,* containing 200 mg of iron^{III}	0.3	0	
2N, containing 200 mg of iron^{III}	8	0.3	0

* Phosphoric acid was present only in the applied solution

A reversible photoreduction of 12-tungstophosphoric acid occurred on exposure of the band on the cellulose to sunlight, providing a means of locating the band. Reduction did not occur, however, when iron was present initially.

(iii). Detailed study of the adsorption behaviour of 12-tungstophosphoric acid and other heteropoly acids

A study was made of the influence of acid concentration and presence of phosphoric acid and iron on the behaviour of 12-tungstophosphoric acid. The effect of boiling solutions of 12-tungstophosphoric acid was investigated, as this was of potential importance for separation from 12-molybdophosphoric acid.

200-Mg amounts of tungsten as 12-tungstophosphoric acid (BDH AnalaR) were applied in 30 ml solutions to columns containing 6 g of cellulose powder. The latter was equilibrated with, and elution effected with, the same concentration of hydrochloric acid as was used in the applied solution. Tungsten was estimated in successive 50 ml fractions of eluate ("iron fraction") after the retention volume of the column had been discarded. Results are given in Table XVI.

It is apparent that, while unboiled 6N hydrochloric acid solution gave excellent retention, slight loss occurred with 2N acid and with 0.5N acid little tungsten was retained by the cellulose. The presence of phosphoric acid had no effect on unheated solutions, but it increased the loss caused by boiling 12-tungstophosphoric acid in 6N hydrochloric acid solution before application to the column. Boiling in 2N hydrochloric acid

did not have an adverse effect. The presence of iron very slightly increased the small initial loss that occurred with 6N hydrochloric acid, and caused a large loss with 2N acid. 6N hydrochloric acid was adopted as eluent for further work.

The behaviour of 12-tungstophosphoric acid in 6N nitric and sulphuric acids was also examined. Excellent retention occurred with both, showing that as well as being possible eluents, these acids could be present in the applied solution. For lead-containing materials nitric acid would be necessary.

12-Molybdophosphoric acid dissolved in cold 6N hydrochloric acid solution, spread over the whole column and was only very slowly eluted. When the solution was boiled briefly before application to the column, molybdenum was completely eluted in the "iron fraction". Thus 12-tungstophosphoric and 12-molybdophosphoric acids could probably be separated. In practice, where molybdate and tungstate would be present during acidification in presence of phosphate, mixed heteropoly acids would be likely to form (37), making separation of molybdenum and tungsten impossible by this method.

The behaviour of 12-tungstosilicic and 12-tungstoboric acids was also examined since these might be present, particularly the former, as heteropoly acids containing silicon as the hetero atom have a greater stability than those with phosphorus (27). Comparable amounts of both acids were quantitatively retained by the columns in 6N hydrochloric acid, less than 0.1 mg of tungsten being eluted in the "iron fraction". It was similarly shown that 18-tungsto-2-phosphoric acid was quantitatively adsorbed from 6N hydrochloric acid solution.

Fluoride had been shown to have an adverse effect on the formation and precipitation of 12-tungstophosphoric acid when polythene vessels were

employed (p. 24), so the influence on the column behaviour was now examined. When a solution of 60 mg of tungsten, as sodium tungstate, was acidified with 0.5 ml of hydrofluoric acid, made up to 6N in hydrochloric acid and passed through a polyvinyl chloride column containing cellulose, no retention of tungsten occurred. Addition of phosphoric acid to the hydrofluoric acid solution did not have any influence.

Various methods of eliminating the effect of fluoride other than by evaporation with phosphoric or sulphuric acid, were now considered. When the fluoride-containing solution was left in contact with silica gel, subsequent retention on the cellulose was considerably increased. This process was too slow for practical use, since standing overnight was required to reduce the loss of tungsten even to 2 mg, and there was a concomitant risk of tungsten being absorbed by silica gel.

Use of borate to complex fluoride as fluoroboric acid (38) was examined. A solution containing 60 mg of tungsten as sodium tungstate, 43 mg of sodium fluoride, 50 mg of disodium tetraborate decahydrate and 26 mg of phosphate was made alkaline with sodium hydroxide and then reacidified with hydrochloric acid. (43 Mg of NaF = 20 mg of F = 25 mg of $Na_2B_4O_7.10H_2O$ in HBF_4; 60 mg of W = 2.6 mg of PO_4 in $H_3PO_4.12WO_3$.) Application to a column resulted in loss of only 0.5 mg of tungsten - a good result since little attention had been given to the conditions of acidification at this stage (cf. p. 67). It was not ascertained if retention of tungsten was partly due to formation of borotungstate, but borate, where necessary, can be eliminated as the volatile methyl borate, by heating with methanol in presence of hydrochloric acid (39). This approach

appeared to introduce unnecessary complications so it was decided to adhere to the previous method of removing fluoride by fuming with phosphoric or sulphuric acid (p.25).

(iv). Study of methods of dissolution of tungsten-containing materials with respect to subsequent separation of iron by cellulose chromatography

Tentative experiments were made with approximately 75-mg amounts of tungsten powder, sometimes with 25 mg of iron added, and with ferrotungsten. Columns, 2 cm in diameter, containing 10 g of cellulose were employed. Methods of dissolution described earlier were used (p.25 et seq.).

Procedure A. Tungsten powder was dissolved with hydrofluoric and nitric acids in presence of 0.3 ml of phosphoric acid and the syrupy residue, left after evaporation, taken up in 10 ml of 6N hydrochloric acid. 25 Mg of $iron^{III}$ were added, the solution was applied to a cellulose column equilibrated with 6N hydrochloric acid and elution effected with acid of the same concentration. By applying the dithiol test (Appendix p. 95), at intervals, to portions of the "iron fraction" it was found that considerable loss of tungsten had occurred. Only 55% was recovered in the tungsten fraction. The bulk of the tungsten lost was in the first 30 ml of effluent, there being a slow continuous loss thereafter. It was considered that fluoride might not have been eliminated by evaporation in presence of phosphoric acid.

When the determination was repeated, but with the addition of 0.1 ml of sulphuric acid, and evaporation to dense fumes effected, precipitation occurred on taking up the residue in hydrochloric acid. It was concluded

that dehydration of orthophosphoric acid had occurred causing precipitation of tungstic acid in the absence of phosphate (PO_4).

In a further experiment, addition of 26 mg of phosphate with the hydrochloric acid kept all the material in solution but considerable loss of tungsten into the "iron fraction" occurred.

Procedure B. Tungsten powder was dissolved in 10 ml of 12N hydrochloric acid and 1 ml of 16N nitric acid in presence of 0.3 ml of phosphoric acid and the solution transferred to a column. No iron was added. On elution, loss of tungsten occurred, there being again a sharp initial expulsion of several milligrams.

It was now apparent that direct dissolution of tungsten in acid was unsuccessful due to incomplete formation of 12-tungstophosphoric acid, and that fluoride and iron were not solely responsible.

Procedure C. Samples of tungsten powder and of ferrotungsten were dissolved by means of hydrofluoric and nitric acids in presence of 0.3 ml of phosphoric acid and the volatile acids evaporated off. 8 Ml of 6N sodium hydroxide solution were added to the residues which were then slowly reacidified with hydrochloric acid in the cold. Acid concentrations were then raised to 6N and the solutions applied to cellulose columns as usual. Several milligrams of tungsten were lost from the column into the "iron fraction" in both experiments.

When the experiment with ferrotungsten was repeated, but with 0.1 ml of sulphuric acid also present in the dissolution mixture containing phosphoric acid, and evaporation was continued to fumes of sulphuric acid,

loss of tungsten still occurred.

In further experiments on ferrotungsten, phosphoric acid was omitted and sulphuric acid substituted for removal of fluoride, before the residue was treated with sodium hydroxide solution. Reacidification in presence of 26 mg of phosphate and application to a column as usual, gave a solution from which only 0.3 mg of tungsten was lost, whereas 4 mg were lost when 850 mg of phosphate had been added. In the experiment with the small amount of phosphate, a little iron remained with the tungsten fraction and was only very slowly eluted with 6N hydrochloric acid.

It was therefore concluded that fluoride had to be removed by fuming with sulphuric acid and that the phosphate concentration had to be kept down.

Procedure D. Tungsten and ferrotungsten were dissolved with hydrofluoric and nitric acids in presence of 0.2 ml of sulphuric acid. After evaporation to remove excess acids, the residue was fused with sodium carbonate. The melt was extracted with water, 26 mg of phosphate as disodium hydrogen phosphate were added and the mixture slowly acidified with hydrochloric acid. With tungsten powder alone, loss of only 0.3% of tungsten (0.2 mg) into the "iron fraction" occurred. The tungsten fraction, which was eluted from the column with 30 ml of 0.2N sodium hydroxide solution containing 26 mg of phosphate, yielded 99.3% of tungsten with tri-n-butylamine. With ferrotungsten 1.5% (1 mg) was lost to the "iron fraction". Difficulty was encountered with ferric oxide, which, after sodium carbonate fusion, was virtually insoluble in hydrochloric acid even on heating. Experiment showed that only bisulphate fusion effectively broke down this material and

1.5% of the tungsten taken was found therein.

Of the four methods of disintegration examined, Procedure C gave the best results, where sulphuric acid was substituted for phosphoric acid and addition of a small amount of phosphate was made afterwards. Procedures A and B were clearly unsatisfactory and with ferrotungsten Procedure D was inferior to Procedure C. The modified Procedure C was therefore adopted.

(v). Detailed study of the conditions of formation of 12-tungstophosphoric acid from tungstate and phosphate

As the behaviour of tungstophosphoric acid formed from tungsten-containing materials differed from that of authentic 12-tungstophosphoric acid, a study was made of conditions of formation of tungstophosphoric acid.

200-Mg amounts of tungsten as sodium tungstate along with varied amounts of phosphate as the disodium hydrogen salt were dissolved in water and 1 ml of 6N sodium hydroxide was added to make the solutions strongly alkaline. The magnetically stirred mixtures were acidified with different concentrations of hydrochloric acid added at a steady dropping rate, until thymol blue indicator turned red. After the acidification, solutions were made up usually to 50 or 60 ml, 6N in hydrochloric acid, and transferred to cellulose columns, 1.5 cm in diameter, containing 6 g of cellulose equilibrated with 6N hydrochloric acid. Elution was effected with the same acid and the effluent collected in 50 ml fractions after the retention volume of the column had been discarded. Results are shown in Table XVII.

It is apparent that, where the criterion for formation of 12-tungstophosphate is adsorption by cellulose in 6N hydrochloric acid, then conditions

TABLE XVII

LOSS OF TUNGSTEN FROM COLUMNS TO WHICH TUNGSTOPHOSPHORIC ACID PREPARED FROM 200 MG OF TUNGSTEN^{VI} AND PHOSPHATE HAD BEEN APPLIED

200 Mg of W = 8.5 mg of PO_4 in $H_3PO_4.12WO_3$

Phosphate (PO_4), mg	Hydrochloric acid for neutralisation, N	Approximate temperature when neutralised, °C	Volume applied to column, ml	Tungsten in 50 ml fractions of effluent mg		
17	2	18	50	2	0.4	0.2
17	2	100	50	0.5	<0.1	0.2
17	6	100	50	0.2	<0.1	0.3
17	6	100	30	0.2	<0.1	0.5
17	12	100	50	0	0.7	1.5
43	6	100	50	0.8	0.4	1.5
85	6	100	50	0.4	2	6
850	2	18	60	4	20	16
850	2	100	60	1	15	11
850	12	100	60	0.3	40	20

of acidification had a considerable influence. Thus, neutralisation of hot solutions with 12N acid almost prevented loss of tungsten in the first fraction of the effluent. When 850 mg of phosphate were present, whether acidification was performed with 2 or 12N acid complete formation of 12-tungstophosphoric acid had apparently not occurred immediately, as judged by the high tungsten content of the second and third portions of the effluent. With 17 mg of phosphate, twice the theoretical requirement for formation of 12-tungstophosphate, best all-over results were obtained. Acidification at the boiling point of the solution was best and results improved so far as initial loss of tungsten was concerned with increasing normality of the acidifying acid, i.e. with increasing rapidity of acidification.

The advantage of rapid acidification was further shown where the same amount of tungstate with 17 mg of phosphate and 8 ml of 6N sodium hydroxide solution was rapidly acidified at room temperature by distillation from hydrochloric acid. 25 ml of 12N hydrochloric acid were boiled in a flask and the evolved vapour distilled into the solution through a delivery tube . Very rapid acidification was thus possible and moreover the volume of solution was kept to a minimum. Loss of only 0.2 mg of tungsten occurred in the first 50 ml of effluent.

It was concluded that rapid acidification in presence of only a small excess of phosphate yielded the best results. To avoid possible complications, such as binding of phosphate by iron, in presence of other metals 43 mg of phosphate (five times the theoretical quantity) was selected as being a suitable amount for use with 200 mg of tungsten.

Because 12-tungstophosphoric acid deteriorated on boiling in 6N

TABLE XVIII

BEHAVIOUR OF 12-TUNGSTOPHOSPHORIC ACID PREPARED UNDER VARIED CONDITIONS

Phosphate present mg	pH at which solution cooled	Tungsten in 50 ml fractions of effluent, mg	
43	4	<0.1	<0.1
43	2	<0.1	<0.1
43*	2	<0.1	<0.1
43	1	0.2	0.1

* Acidification by distillation from 12N hydrochloric acid into solution at 18°C.

hydrochloric acid (p. 61) it was impracticable to acidify solutions rapidly in the hot and straightway make them up to 6N in hydrochloric acid. Experiments were made to determine whether the pH at which the solutions were cooled before making them 6N in acid, was critical.

200-Mg portions of tungsten as tungstate and 43 mg of phosphate were dissolved, 4 ml of 12N sodium hydroxide solution added and the hot solutions acidified with 12N hydrochloric acid added rapidly from a burette. At the pH indicated in Table XVIII the solutions were cooled before making them 6N in hydrochloric acid.

The increased loss when the solution was cooled at pH 1 is probably not significant and it appeared to be unimportant at which stage cooling was carried out, at least, within the range pH 4 to 1. It remained to be shown what effect the presence of other elements, particularly iron, had on the subject.

(vi). Critical experiments on the formation of 12-tungstophosphoric acid from tungstate and phosphate in presence of iron^{III}

Conditions that had been evolved for the formation of 12-tungstophosphoric acid from tungstate and phosphate were now applied in the presence of iron^{III}.

200 mg of tungsten as tungstate in 20 ml of solution were added to 100 mg of iron^{III} as sulphate, 0.7 ml of concentrated sulphuric acid and 6 ml of 12N sodium hydroxide solution. Phosphate was added to the hot, stirred solution followed by 12N hydrochloric acid rapidly from a burette, until hydrated ferric oxide was significantly dissolving (pH~1). The

TABLE XIX

BEHAVIOUR OF 12-TUNGSTOPHOSPHORIC ACID PREPARED FROM TUNGSTATE AND PHOSPHATE IN PRESENCE OF IRON

200 Mg of W = 8.5 mg of PO_4 in $H_3PO_4.12WO_3$

Cellulose in column	Phosphate present,	Iron present,	Tungsten in 50 ml fractions of effluent	
g	mg	mg	mg	
6	43	100	0	>6
6	43	100	<0.1	2.4
6	43	100	0.1	5
6	43*	100	0	4
6	43†	100	0.2	0.3
10	43	100	<0.1	<0.1
10	43‡	100	0.3	0.1
10	43§	100	0.6	0.1
10	17	200	<0.1	<0.1
10	430	200	0.5	0.7

* Acidification at 40°C.

† Acidification by distillation from hydrochloric acid into solution at 18°C.

‡ Rapid acidification until solution was 2N in hydrochloric acid.

§ 12N hydrochloric acid added all at once.

presence of the precipitate prohibited the use of indicators for stopping at higher pH values. The cooled solution was doubled in volume with the same acid, recooled and applied to a column containing 6 g of cellulose as before. The results are given in the upper part of Table XIX. Considerable loss of tungsten in the second part of the "iron fraction" occurred consistently. This confirmed the earlier finding that retention of tungstophosphate by cellulose decreased in the presence of iron (p. 62). Use of longer columns (2 cm in diameter) containing 10 g of cellulose, overcame this difficulty (lower part of Table XIX).

Previous deductions concerning suitable conditions of formation of tungstophosphoric acid were confirmed. Thus 17 to 43 mg of phosphate were satisfactory for 200 mg of tungsten, whether or not 100 to 200 mg of iron were present, but 430 mg caused slight loss of tungsten. Rapid addition of acid from a burette, even until the solution was 2N in hydrochloric acid, caused no significant loss. Ultra rapid acidification where the 12N acid was added all at once to the stirred solution caused only a slightly increased loss. Acidification of the cold solution by distillation from concentrated hydrochloric acid was also reasonably satisfactory. This information showed that the conditions of formation of 12-tungstophosphoric acid had sufficient latitude for practical use.

Retention of a small amount of iron with tungsten almost invariably occurred, where tungstophosphoric acid was formed in presence of iron. Under no conditions where satisfactory retention of tungsten occurred was it possible to elute all residual iron. Not more than 2 mg of iron were found in the tungsten fraction. Where tungstophosphate was formed in

presence of large amounts of phosphate, e.g. 430 mg, this effect was much reduced. Heating the tungstophosphate in 6N hydrochloric acid solution up to 70°C or higher for a few minutes also permitted almost complete removal of iron, but loss of tungsten into the "iron fraction" then occurred. Fortunately, 2 mg-quantities of iron could readily be rendered innocuous by reduction with ascorbic acid (p. 52).

The use of quantities of iron greater than 200 mg was not examined although tentative experiments showed that 400 mg could possibly be tolerated in the procedure. Where more iron was present, difficulty was encountered due to the bulky precipitate of hydrated ferric oxide.

In attempts to avoid precipitation of iron in alkaline solution, the addition of various complexing agents was tried. Citrate, tartrate and oxalate all had a complexing effect on tungsten and interfered. Of the more specific chelating agents, bishydroxyethylglycine and triethanolamine satisfactorily complexed iron under the required strongly alkaline conditions. Triethanolamine however precipitated 12-tungstophosphate (p. 13). The iron complex with bishydroxyethylglycine, under suitable conditions for formation of 12-tungstophosphate, was broken down on heating, resulting in precipitation of hydrated ferric oxide. Acidification was therefore done in the cold using distillation from 12N hydrochloric acid (p. 69). When the complexing agent was used no loss of tungsten into the "iron fraction" subsequently occurred during the separation procedure. As there appeared to be no particular necessity to keep up to 200 mg of iron in solution, and as the iron complex broke down very readily on heating, this work was not pursued further.

Rapid acidification with 12N hydrochloric acid of hot solutions containing 43 mg of phosphate was therefore adopted for up to 200 mg of tungsten^{VI}.

(vii). Conversion of tungsten into 12-tungstophosphoric acid in the presence of iron^{III} and determination with tri-n-butylamine

Preparation of cellulose columns A 20 mm internal diameter Pyrex glass tube was attached to a 2 mm capillary stopcock, and fitted with a perforated porcelain disc. The column was 24 cm long and had 12 cm of 2 mm-bore capillary below the tap, and was so constructed as to have the minimum of dead space between disc and barrel of stopcock.

A circle of Whatman No. 41 filter paper rested on the disc, on top of which 10 g of cellulose powder were added as a slurry in 6N hydrochloric acid, which in turn was surmounted by another disc of filter paper. This hydrochloric acid suspension gave better packing than one in water. The column was recycled before use by adding successively 30 ml of water, 30 ml of 0.2N sodium hydroxide solution and 50 ml of 6N hydrochloric acid. The flow-rate of the 10 g column was about 2 ml per minute and was increased to 3 to 5 ml, where necessary, by means of suction or, preferably, slight pressure. This was applied to the top of the column from an aspirator maintained at constant pressure by a head of water that could be varied as required to provide a suitable flow rate. Columns did not drain below the top circle of paper when run under atmospheric pressure alone.

When cellulose was left for any length of time in contact with 6N hydrochloric acid subsequent elution with dilute sodium hydroxide solution caused loss of cellulosic material which precipitated slowly in the

reacidified solution. This was avoided in quantitative experiments by equilibrating the column with 6N hydrochloric acid immediately before use and by not delaying elution of the adsorbed tungstophosphoric acid. Several milligrams of degradation product were eluted after 2 hours' contact of cellulose and acid.

Columns were used a dozen times or more before rejection, life apparently being restricted only by the closer packing and the diminished flow rate caused by degradation of the cellulose. When not in use, cellulose was left under water, but where accidental drying out occurred repacking of the same material was permissible. Silicone treatment of the column walls did not stand up to the action of the dilute sodium hydroxide solutions, and was not used.

Method for tungsten. To a solution containing 50 or 200 mg of tungsten as tungstate and 200 mg of iron^{III} as sulphate, 0.7 ml of 36N sulphuric acid was added. The stirred solution was made up to 20 ml, 6 ml of 12N sodium hydroxide solution were added, and, after heating to about 80°C, 45 mg of phosphate as the disodium hydrogen salt were added, followed by 12N hydrochloric acid added rapidly from a burette until hydrated ferric oxide was significantly dissolving. The solution was cooled, the volume doubled with the same acid, and, after recooling, added to a cellulose column previously equilibrated with 6N hydrochloric acid. Sodium chloride precipitated out while the solution was being cooled to room temperature. Cooling before transferring to the column was essential as, otherwise, clogging of the pores of the disc of filter paper was capable of blocking

TABLE XX

DETERMINATION OF TUNGSTEN IN THE PRESENCE OF IRON

Tungsten taken, mg	Tungsten found, mg	Tungsten found in "iron fraction", mg
200.0	200.2	< 0.2
200.0 *	200.2	< 0.1
50.0	49.9	~ 0.2
50.0	49.7	~ 0.1

* Only 17 mg of phosphate were present during initial acidification.

the column. Washing, and elution of the "iron fraction", were effected with 50 ml of 6N hydrochloric acid, followed by 20 ml of water in order to reduce the acid concentration of the tungsten fraction. The first 30 ml of effluent, the retention volume of the column, were discarded and the remainder, the "iron fraction" tested for tungsten with dithiol (Appendix (p. 95). The tungsten fraction was then eluted with 30 ml of 0.2N sodium hydroxide solution followed by 30 ml of water. The solution was made alkaline with 12N sodium hydroxide solution and 2 ml excess added, before acidifying in presence of phosphate as above, but with thymol blue as indicator. Water and hydrochloric acid were added to make the volume up to 100 ml, N in hydrochloric acid. 100 Mg of ascorbic acid were added to the hot solution and when any yellow coloration had disappeared, tri-n-butylamine reagent was added. The precipitate was separated and weighed as described on p. 20. Results are shown in Table XX.

The method was considered to be satisfactory for determination of up to 200 mg of tungsten in the presence of 200 mg of iron.

7. Study of the Behaviour of Some Other Interfering Elements

(i). Manganese

As was indicated previously (p. 36) manganese when present during formation of 12-tungstophosphoric acid gave a contaminated precipitate unless ascorbic acid was used, probably because traces of manganese^{III} behaved in a similar fashion to iron^{III}. Since manganese^{III} gave a purple coloration in presence of tungstophosphoric acid, it was concluded to be a manganese tungstophosphate (31). In experiments involving cellulose column separations, this material formed a purple band which travelled slightly ahead of the main tungstophosphoric acid one. Under the conditions developed this band was not eluted, although with 200 mg of tungsten as tungstate and 200 mg of manganese, 0.6 mg of tungsten was obtained in the "iron fraction". The remaining tungsten was not determined since it had already been shown that ascorbic acid would prevent interference of accompanying manganese (p.36). Thus manganese did not seriously interfere in the separation and determination, provided ascorbic acid was added before precipitation with tri-n-butylamine.

(ii). Chromium

Only trace amounts of chromium occur in ores and minerals, and minor amounts in most tungsten steels. Small amounts nevertheless were shown to interfere in the precipitation of 12-tungstophosphate with tri-n-butylamine (p. 33). Where chromium^{III} was present only part redissolved after the alkaline treatment and during the cellulose column separation procedure, considerable loss of tungsten into the "iron fraction" occurred. Other methods of dealing with chromium were considered.

Since chromate was not likely to interfere in the formation of 12-tungstophosphate, chromium^{III} was oxidised before formation of the heteropoly acid. 25 Mg of chromium^{III} chloride in presence of 200 mg of tungsten^{VI} were treated as in the described method (p. 76), except that several drops of bromine were added to the alkaline solution and chromate was formed by warming. Thereafter, the solution was acidified and the usual column procedure followed. Both chromate and excess bromine were collected in the "iron fraction". Tungsten recovered by means of tri-n-butylamine was 99.9% and no loss into the "iron fraction" occurred. Quantities of chromium much greater than 25 mg were not readily dealt with in the above fashion. Such amounts might possibly be eliminated by volatilisation as chromyl chloride (40). Possible complications due to oxidation of cobalt, nickel and manganese by bromine were not examined.

(iii). Molybdenum

Although 12-tungstophosphoric acid could probably be separated from 12-molybdophosphoric acid (p. 57), mixed heteropoly acids are formed when tungstate and molybdate are acidified in presence of phosphate (37). Moreover 12-molybdophosphate is precipitated by tri-n-butylamine and the mixed heteropoly acid would, most probably, also be precipitated by this reagent. In the present work, therefore, tungsten cannot be determined in the presence of molybdenum.

(iv). Vanadium

Where precipitation of 12-tungstophosphate was effected in presence of vanadium^{V}, a deep yellow coloration was imparted to the precipitate with

tri-n-butylamine (p. 34). If vanadium^{V} was present during formation of tungstophosphate, in the subsequent cellulose column procedure a large orange band spread over the entire column and caused loss of tungsten into the "iron fraction". Vanadium may form mixed heteropoly acids with tungsten^{VI} and phosphate (41), prohibiting the application of the method in its presence.

(v). Tin

While 12-tungstophosphoric acid formed in the presence of 25 mg of tin^{IV} and precipitated directly with tri-n-butylamine gave a small positive error (p. 35), when the column procedure was used 99.5% of the 200 mg of tungsten^{VI} taken, was apparently recovered with tri-n-butylamine and 0.9% was found in the "iron fraction". Thus only small amounts of tin can be tolerated.

(vi). Tantalum and niobium

High results were obtained with 5 mg of both tantalum and niobium in the direct precipitation (p. 35) and also in the column procedure where 102.8% of the 200 mg of tungsten was now found with a loss of 0.1% to the "iron fraction". Very little of these metals can thus be tolerated.

The method so far developed can be applied to materials containing only insignificant amounts of molybdenum, vanadium, tantalum, niobium and titanium (p. 35) and small amounts of tin, chromium and possibly aluminium (p. 35). Other elements which may be present in quantity are calcium, cobalt, copper, lead, manganese and nickel (p. 36) and iron (p. 78).

8. Determination of Tungsten in Ferrotungsten, Scheelite and Wolframite

British Chemical Standard ferrotungsten No. 242, containing 81.28% of tungsten, 0.10% of tin and 0.028% of sulphur was used. Samples of scheelite and wolframite, kindly supplied by the late Dr. A. M. Cockburn of Edinburgh University, were analysed by classical procedures, quantitatively for tungsten and semi-quantitatively for elements commonly present that might interfere. Page references given in parenthesis,[ ], below, relate to W. R. Schoeller and A. R. Powell, "Analysis of Minerals and Ores of the Rarer Elements", (Griffin, London, 3rd Ed., 1955).

Examination of scheelite (essentially calcium tungstate)

Tungsten was determined in 500mg of material by the aqua regia - ammonium tungstate method [p. 287]. Scheelite ground to 100 mesh was digested with hydrochloric and nitric acids with formation of tungstic acid. Addition of cinchonine completed the precipitation of tungsten and the solid residue was separated. The filtrate contained no titanium and very little iron when tested with hydrogen peroxide and thiocyanate, respectively. Tungstic acid was dissolved in ammonia, which was then evaporated off, and tungsten determined as the ignition product, tungsten trioxide. This purified tungstic oxide was examined for silicon and phosphorus (Appendix p. 96), and small corrections were applied. All but 8 mg of residue from the ammonia extraction of the crude tungstic oxide was volatilised by means of hydrofluoric acid in presence of sulphuric acid and was therefore silica, of which the mineral was found to contain altogether about 25%. The remaining residue contained so little tungsten that it was fused with sodium carbonate

and the aqueous extract tested appropriately with dithiol (Appendix p. 95).

Fresh portions of mineral were tested for molybdenum by the thiocyanate reaction [p.267 (c)], and, after removal of silica, for tin by using hydrogen sulphide [p. 290, (a),(1)]. Molybdenum was absent but tin was probably present, since an insoluble residue remained in the tartaric acid extract of the bisulphate melt [p. 202,(a)], although the amount was small enough to be ignored. Tantalum and niobium were sought in a 200-mg sample that was first freed from silica and the bulk of the tungsten, as described above. The residue was fused with potassium bisulphate and tested with tannin in dilute sulphuric acid solution [p. 207, (h),(1)]. A dark brown precipitate, resembling neither the tantalum nor the niobium complex, compared in bulk with the precipitate obtained from 0.2 mg of niobium.

Examination of wolframite (an iron - manganese tungstate)

500 Mg of mineral, ground to 240 mesh, were analysed for tungsten as described above. A 15 mg residue, mainly undecomposed material, left after removal of tungstic acid and silica, was fused with potassium carbonate. Tantalum and niobium in the aqueous extract, along with an insoluble brown residue from the carbonate fusion, were collected by the magnesia method [p. 206, (g),(1)] and the residual tungsten was recovered (10.5 mg of tungsten trioxide) with tannin and cinchonine [p. 283, (c)]. The brown residue was dried, ignited and fused with potassium bisulphate, and the cooled melt extracted with N sulphuric acid. The solution was found to contain 0.5 mg of iron, 1 mg of manganese and no titanium, using thiocyanate, periodate and hydrogen peroxide respectively. A white residue was fused

with potassium bisulphate and 0.5 mg of niobium detected with tannin [p. 207, (h),(1)]. Approximately 0.1% of molybdenum was found in a separate portion of mineral [p. 267, (c)].

From the above results it was concluded that tungsten could be determined in both minerals as tris(tri-n-butylammonium) 12-tungstophosphate, and that the cellulose-column separation procedure was unnecessary for the scheelite.

Procedure for ferrotungsten

Not more than 200 mg of tungsten should be present. To a suitable amount of material in a 25 ml platinum crucible were added 1 ml of hydrofluoric acid (40%) and 1 ml of concentrated sulphuric acid. 1 drop of concentrated nitric acid was added and the crucible gently heated if necessary to initiate the reaction. More nitric acid was added continuously until disintegration was complete. Hydrofluoric and nitric acids were expelled by heating the crucible at a controlled temperature in a metal block or on a hot-plate, and finally at higher temperature over a micro-bunsen burner, until sulphuric acid fumed strongly. After cooling, the contents of the crucible were transferred to a beaker by means of a minimum volume of water and four 1 ml rinsings, alternately with 2N sodium hydroxide solution and 2N hydrochloric acid solution. The volume at this stage was about 20 ml and in no case exceeded 25 ml. 12N sodium hydroxide solution was added to the magnetically stirred solution until precipitation of

hydroxides was complete and a 2 ml excess was present. The solution was heated to about 80°C and 160 mg of hydrated disodium hydrogen phosphate (43 mg of phosphate) were added. Finally, while maintaining the heating, 12N hydrochloric acid was added rapidly dropwise until hydrated ferric oxide was just dissolving (pH~1). Further heating and stirring gave complete solution, although, if necessary, increasing the acidity of the hot solution to 2N was permissible (Table XIX).

Before transfer to a suitably prepared column (p. 75), the acid concentration of the cooled solution was raised to 6N by adding 12N acid. The beaker and column were washed with 50 ml of 6N acid and then the column was washed with 20 ml of water. Tungstophosphoric acid was eluted from the column with 30 ml of 0.2N sodium hydroxide solution and 30 ml of water. The eluate was neutralised with 12N sodium hydroxide solution and 2 ml of excess added, followed by phosphate and 12N hydrochloric acid, as above, until the pH was ~1 (thymol blue indicator). At this point the volume was increased to 90 ml with water and the acid concentration to N, 100 mg of ascorbic acid were added to the hot solution and the tri-n-butylamine complex was precipitated and weighed as previously described (p. 20).

Procedure for minerals

To a sample containing up to 200 mg of tungsten, 3 ml of hydrofluoric acid and, after 15 minutes, 1 ml of nitric acid were added. The crucible was gently heated on a temperature-controlled hot-plate, then cooled and 1 ml of concentrated sulphuric acid added cautiously. Thereafter in analysing wolframite, the method for ferrotungsten was followed. With

TABLE XXI

DETERMINATION OF TUNGSTEN IN FERROTUNGSTEN, SCHEELITE AND WOLFRAMITE

Material	Tungsten found by new method %	Tungsten found by classical methods %
Ferrotungsten	81.9 81.9	81.3 *
Scheelite	44.3 44.4	44.6 44.9 (56.4% WO_3)
Wolframite	59.1 59.2	60.0 59.9 (75.6% WO_3)

* Certificate value.

scheelite, the column separation was omitted and instead, after forming tungstophosphoric acid in the hot solution (pH~1), the volume was made up to 100 ml, N in hydrochloric acid, ascorbic acid added and tris(tri-n-butylammonium) 12-tungstophosphate precipitated.

The results for the three materials are given in Table XXI.

While precise results are obtained by the new method, they are not identical with those obtained by classical methods. The certificate value for ferrotungsten, which is the average of several independent analyses, can probably be relied upon. The small amount of tin known to be present would not significantly affect the determination of tungsten with tri-n-butylamine, but if, for example, a little tantalum or niobium were present, a positive error would be expected. In the certificate it is not specifically stated that tungsten, iron and tin are the sole metallic constituents of the material. For the minerals, the values obtained by classical procedure are less certain on account of the many other elements present and the necessary separations and corrections entailed.

Particularly with minerals, the new method is appreciably shorter than the classical one and a result for tungsten is obtained directly. It is unnecessary to examine for residual traces of tungsten, provided the disintegration is carried out carefully.

DISCUSSION

The formation and stability of 12-tungstophosphoric acid

The formation of tungstophosphoric acid in order to prevent precipitation of tungstic acid in acidified solutions is an accepted analytical method (26). It is used, for example, in the volumetric determination of silicon in tungsten bearing alloy steels, the heteropoly acid being formed by the direct action of hydrochloric and phosphoric acids and an oxidant on the metal. Weiner and Boriss (51) stated that $P(W_2O_7)_6^{7-}$ - 12-tungstophosphoric acid - was probably formed when phosphoric acid was used to prevent separation of tungstic acid from hydrochloric acid solutions before tungsten^{VI} was reduced in a silver reductor. In most cases the exact composition of the heteropoly acid may not be of importance but it is usually assumed that 12-tungstophosphoric acid is formed and that quantitative conversion is fairly readily achieved, although Duval's statement (p. 4) is not in agreement with this.

In the present work precipitation of tungstophosphate with tri-n-butylamine (Table III, p. 19) has shown that 12-tungstophosphoric acid is apparently readily formed when a solution of tungstate and an excess of phosphate is acidified. Thus, crystallised 12-tungstophosphoric acid gave essentially the same results (yield of precipitate, loss of tungsten to the filtrate and percentage of phosphorus in the precipitate) as heteropoly acid formed after degrading the original material to phosphate and tungstate with an excess of sodium hydroxide, and reacidifying the solution in presence of a 10-fold excess of phosphate. The rate of acidification and the actual excess of phosphate appeared not to be critical.

It could not be assumed, however, that dissolution and oxidation of tungsten in acid solutions containing phosphoric acid would lead to 100% formation of 12-tungstophosphoric acid and recovery as tris(tri-n-butylammonium) 12-tungstophosphate. Results given in Table VI, p. 26, indeed show that discrepancies occurred although these were not large.

The apparent high total recovery of tungsten could perhaps be attributed to formation of some 18-tungsto-2-phosphoric acid, which readily precipitated quantitatively with tri-n-butylamine (p. 28). The presence of 10% would increase the weight of precipitate by only 0.6%. Thistlethwaite's remarks on ammonium phosphomolybdate (52), that not only precipitate weight but also the ammonium, molybdenum and phosphorus contents should be examined in each experiment, could also be applied here although the tris(tri-n-butylammonium) 12-tungstophosphate complex is not affected by conditions to nearly the same extent (53). Classical methods of analysis however may not be sufficiently accurate to detect small divergences from 12-tungstophosphoric acid. Loss of tungsten to filtrates could be caused by degradation of the heteropoly acid to tungsten compounds that were not precipitated by tri-n-butylamine.

These difficulties were resolved by completely degrading the heteropoly acids at high pH and then reacidifying the solutions before precipitation with the amine (Table VII, p. 30). It was therefore concluded that 12-tungstophosphoric acid had to be formed by acidifying an alkaline solution containing simple tungstate and phosphate ions.

Later, when attempts were made to separate iron from tungstophosphoric acid chromatographically by adsorbing the heteropoly acid from

6N hydrochloric acid solution on a column of cellulose, it was found that a heteropoly acid showing the same adsorption characteristics as authentic 12-tungstophosphoric acid could not be prepared by direct acid treatment of tungsten (p. 64). Unexpected difficulty was also experienced in obtaining the required heteropoly acid by acidifying alkaline solutions containing tungstate and phosphate with hydrochloric acid and then raising the acid concentration of the cold solution to 6N for the column procedure (p. 67).

Two kinds of irregular behaviour were noted, viz., sharp initial expulsion of several milligrams of tungsten from the column followed by slow continuous loss on elution with 6N hydrochloric acid, and/or accelerated travel of tungsten on the column. Although more concentrated solutions had been used in order to keep volumes small, they were not thought to be a source of error. The critical factors were found to be the concentration of phosphate and the rate of acidification. Rapid acidification with concentrated hydrochloric acid of briskly stirred, hot alkaline solutions, which were then made 6N in hydrochloric acid in the cold prevented the initial sharp loss of tungsten when the solutions were transferred to the columns. The presence of only a small excess of phosphate before acidification prevented subsequent very rapid travel of tungsten on the column.

Heating strongly acid solutions of tungstophosphoric acid was not permissible. Jander and Exner (54), as a result of dialysis measurements, deduced that 12-tungstophosphoric acid in strongly acidified solutions can degrade to give compounds of the basic tungstyl ion WO_2^{++} particularly in dilute tungsten solutions. No excess of phosphate was present in Jander and Exner's work. Spitsyn and Matyazh (55) state that 12-tungstophosphoric

acid is not broken down by 1 to 12N hydrochloric acid even when left 1 to 2 days at boiling temperature. Although they mention in the introduction to their paper the possibility of tungstyl compounds being formed, they take the absence of precipitation of tungstic acid and constancy of the tungsten and phosphorus content as being sufficient evidence of stability. Degradation to tungstyl and phosphate ions would neither cause precipitation nor alter the analytical results. There is thus some doubt whether the heteropoly acid was degraded or not. It was found in the present work that boiling a 6N hydrochloric acid solution of 12-tungstophosphoric acid for 20 minutes produced a small amount of tungsten compound that was not absorbed by cellulose and that more was left unadsorbed when the solution also contained some phosphoric acid (Table XVI, p. 60). Tungstophosphoric acid produced directly from tungsten in hot concentrated acid solutions (p. 64) was therefore incompletely adsorbed by cellulose because of this degradation process. Formation of 18-tungsto-2-phosphoric would not explain the results, as this acid was readily adsorbed by cellulose (Table XIV, pp. 54, 62).

The mechanism of formation of tungstophosphoric acid (56) involves the formation of the paratungstate anion from the tungstate ion at a pH below 6. To explain differences between fresh and aged solutions at pH 6, Souchay suggested that in solution there is an equilibrium between two species of paratungstate ions, which may differ structurally or in respect of hydration. Paratungstate A is formed by a rapid reaction between WO_4^{2-} ions and H^+ ions, and is reactive towards hydrogen ions etc. Paratungstate B is the anion present in the crystalline salts and reacts only through its slow intermediate conversion to paratungstate A.

$$WO_4^{2-} \xrightarrow{pH\ 6} [HW_6O_{21}]^{5-} \rightleftharpoons [HW_6O_{21}]^{5-}$$

Paratungstate A Paratungstate B

At a pH around 4 a further reaction ensues leading to the pseudo-metatungstate anion. This is structurally distinct from the paratungstate ions and as it persists in fairly high acid concentration, it is probably the species which reacts with other acids to form the heteropoly tungstates.

$$[HW_6O_{21}]^{5-} \xrightarrow{pH\ 4} [H_3W_6O_{21}]^{3-}$$

Paratungstate A Pseudo-metatungstate

Rapid acidification in the present work is probably necessary to minimise formation of paratungstate B.

While Jander and Exner (54) suggested that the pseudo-metatungstate reacted with phosphate at increasing acidity to form 12-tungstophosphoric acid passing through a 6-tungstophosphoric acid as an intermediate, Souchay (29) disputed the presence of a 6-tungstophosphoric acid but showed that an 11-tungstophosphoric acid was an intermediate.

In a recent study of the mechanism of formation of 12-tungstophosphoric acid by Ripan, Duca and Stanescu (57), paper chromatography was used with either water or saturated sodium chloride solution at varied pH values as the mobile phase. With saturated sodium chloride solution, tungstate travelled at the solvent front while 12-heteropoly acids remained at the start. They showed that a solution of tungstate acidified to a pH 1.6 or 2 gave in presence of a 12-fold excess of phosphate a heteropoly acid with a 6:1 ratio of tungsten to phosphorus, in presence of a four-fold excess of phosphate a 9:1 ratio and in presence of a three-fold or less excess of phosphate a 12:1 ratio as in 12-tungstophosphoric acid. Under the conditions

used, formation of these species was not quantitative. Unfortunately for comparison with the present work, solutions more acid than pH 1 were not examined. Nevertheless from this paper it would appear that presence of only a small excess of phosphate in the preparation of 12-tungstophosphoric acid for adsorption on cellulose might be necessary to avoid formation of heteropoly acids with a low ratio of tungsten to phosphorus. The effect of small amounts of these on the precipitation with tri-n-butylamine might not be so marked.

12-Molybdosilicic acid has been extensively studied and Strickland (58) has shown that two forms exist. It is possible that 12-tungstophosphoric acid also exists in two forms of similar chemical properties giving rise to the same weight of precipitate with tri-n-butylamine but having different adsorption properties leading to losses from the cellulose columns. The stable α-molybdosilicic acid is formed at low acidities and the β-molybdosilicic acid is formed at high acidities. Strickland suggested that the β-form might be a polymer and that in solution it slowly changed to the α-form by an irreversible depolymerisation. If polymerisation should be a requisite for adsorption of 12-tungstophosphoric acid by cellulose then the necessary rapid acidification might, by minimising conditions of low acidity, avoid formation of the monomer. However, aged tungstophosphoric acid was better retained by cellulose and would, continuing the analogy, be largely monomer. Insufficient information is available in order to form any definite conclusions.

The interference of iron

While heteropoly complexes can be formed with iron as the heteroatom (56),

the presence in the precipitate of the required amount of phosphorus for a 12-tungstophosphate led to the formulation of the iron-containing tri-n-butylamine complex as $\left[Fe(H_2O)(C_{12}H_{27}N)_5\right]PW_{12}O_{40}.2H_2O$. Such a structure is similar to that suggested by Furman and State (59) and modified by Horan (60) to $\left[Co(NH_3)_5H_2O\right]PMo_{12}O_{40}.4H_2O$ for the precipitation of 12-molybdophosphate with nitratopentammine cobalt^{III} nitrate solution. However, the retention of a small amount of iron in the tungsten band on the cellulose column when tungstophosphate had been formed in presence of iron may be due to an iron-tungsten complex. Attempts to separate the residual trace of iron were unsuccessful. Heating the solution prior to addition to the column allowed all the iron to be eluted but loss of tungsten also occurred. There was less iron associated with the tungsten when a larger amount of phosphate was present during formation of the heteropoly acid. Mair (61) has described an 11-tungstoferric^{III} acid, $H_{10}(Fe_2W_{22}O_{74})$, that may possibly be responsible. This acid is stable in cold strong acids and bases but breaks down on heating.

Note: A paper has been published "The Determination of Tungsten as Tris(tri-n-butylammonium) 12-Tungstophosphate", MILLER and THOW, Analyst, 1960, 84, 440, and a short communication "Interference of Iron in the Determination of 12-Tungstophosphoric Acid with Tri-n-butylamine", MILLER and THOW, Talanta, 1960, 5, 128. A paper, "Determination of Tungsten in Association with Iron and Some Other Elements as Tris(tri-n-butylammonium) 12-Tungstophosphate" has been submitted to the editors of Talanta.

APPENDIX

Analytical Procedures

(i). Estimation of tungsten in filtrates and in effluents from columns of cellulose

Quantities of tungsten up to several milligrams were estimated semi-quantitatively by the slightly modified procedure of Miller (42).

Attempts were made, at first, to eliminate organic matter by adding nitric, phosphoric and sulphuric acids to portions of solutions and heating until nitric acid was expelled. In presence of tri-n-butylamine foaming occurred, and, in addition, solutions developed a permanent brownish coloration which made subsequent detection of tungsten difficult. The following method was adopted for nitrate-free solutions.

A volume of solution containing not more than 25 μg of tungsten was evaporated as far as possible in the presence of 0.05 ml of phosphoric acid on a water-bath, an air current being used to expedite evaporation. 0.1 Ml of sulphuric acid, 1 ml of concentrated hydrochloric acid and 0.25 ml of amyl acetate were added, followed by 10 to 20 mg of the zinc salt of toluene-3:4-dithiol (43). The mixture was kept at 70°C for 10 minutes with intermittent shaking, whereupon 1.25 ml of carbon tetrachloride were added and comparison of the blue organic layer effected against standards. Standards with 2,5,10,15 and 20 μg-amounts of tungsten were prepared and, after removal of hydrochloric acid and washing with water, they kept indefinitely.

Oxidising ions such as iron^{III}, were reduced by adding stannous chloride

and warming before addition of dithiol. Tri-n-butylamine and ascorbic acid, in the amounts present in the experiments, were shown not to interfere.

Nitric acid must be removed before applying the dithiol reaction. As the usual method of removal (see above) could not be applied in presence of tri-n-butylamine, and as only a few experiments were done with nitric acid solutions, it was thought that it was scarcely worthwhile working out a special procedure for these.

Where only 1 or 2 μg of tungsten were detected in portions of solution and this indicated less than 0.1 mg in the complete solution, estimations were not generally carried out, and results are indicated as "<0.1 mg".

(ii). Estimation of phosphorus in tungstophosphate complexes.

Phosphorus was estimated colorimetrically as vanadomolybdophosphate, essentially as described by Center and Willard (44). Precipitates (~300 mg) were ignited, fused with 0.5 g of sodium carbonate and the melts extracted with water. After separation from any insoluble hydroxides present, solutions were made up to 100 ml. 20 Ml aliquots were diluted to 80 ml, 2 ml of concentrated sulphuric acid, 5 ml of 0.25% ammonium vanadate solution and 5 ml of 20% ammonium molybdate solution successively added and the solutions made up to exactly 100 ml. Between 30 minutes and 1 hour after preparation, the intensities of the yellow colorations relative to standards were estimated spectrophotometrically.

When tungsten was present, no precipitation of tungstic acid occurred, but a weak yellow coloration developed before addition of the molybdate reagent. Examination of the absorption spectra given by a blank solution,

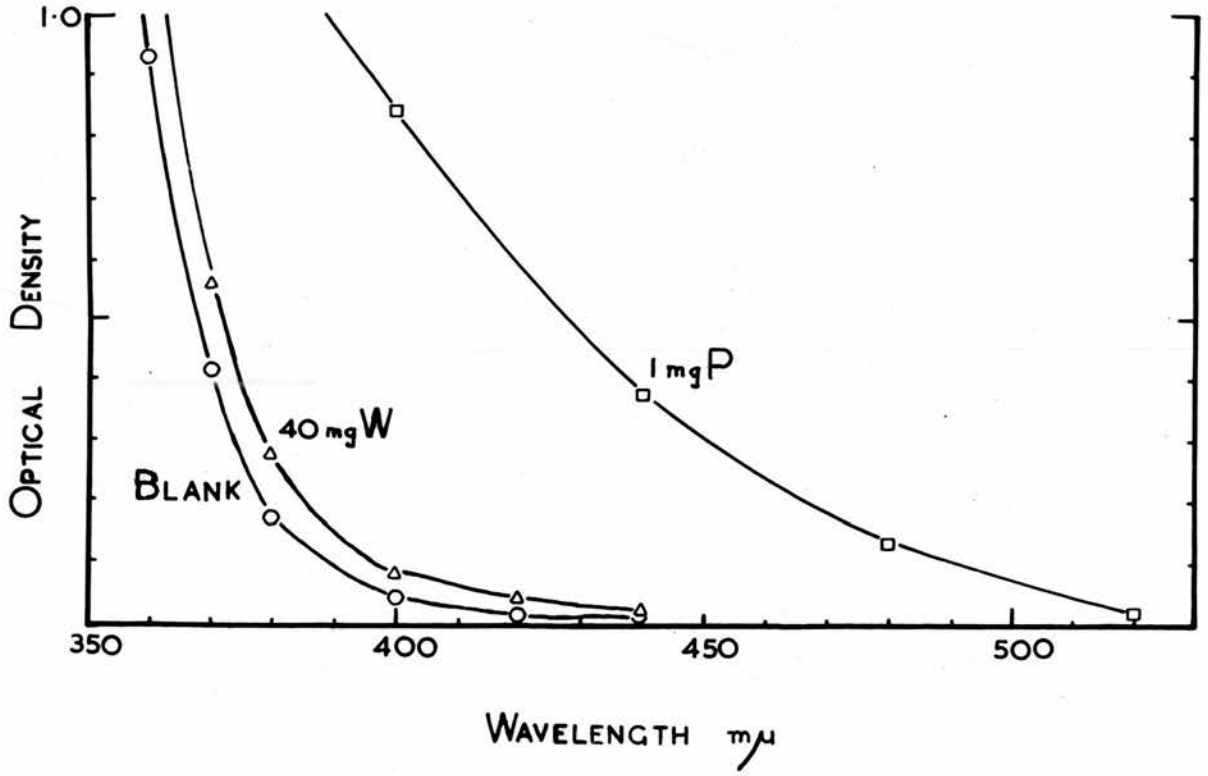
1·0
OPTICAL DENSITY
1 mg P
40 mg W
BLANK
350
400
450
500
WAVELENGTH mμ

Figure 5.

one containing tungstate and another containing 1 mg of phosphorus was made (Fig. 5).

A wavelength of 440 mμ was selected for use, as, although sensitivity for phosphorus was not at a maximum, interference of tungsten was significantly reduced. (Center and Willard used 450 mμ.)

Standards were prepared, each containing 40 mg of tungsten^{VI}, approximately the amount present in the aliquots of the solutions of the precipitates examined. A linear calibration graph was obtained for 0 to 1 mg of phosphorus. Intensity of coloration slowly increased with time but no appreciable error resulted by taking readings in the time range already specified.

(iii). Determination of iron in precipitates with tri-n-butylamine

In the early, more critical experiments for determination of the composition of the substances precipitated, a semimicrogravimetric procedure was used. About 300 mg of precipitate was ignited to constant weight in a 6 ml platinum crucible, then fused with an excess of sodium carbonate and the melt extracted with water. The solution was removed from the hydroxide residue by means of a Miller filter-stick (45) and, after washing, residue and filter pad were ignited in the crucible and the weight of ferric oxide was determined.

For semi-quantitative estimation, hydroxide precipitates were separated by centrifuging, dissolved in hydrochloric acid and the solutions either passed through a small silver reductor for determination of iron^{II} with standard ceric sulphate solution (46), or examined colorimetrically with thiocyanate.

(iv). Determination of carbon and hydrogen in tungstophosphate complexes

A rapid combustion apparatus similar to that recommended by Belcher and Ingram (47) was used for the analysis of 7 to 17 mg portions of complexes in which the amount of organic material ranged from 2 to 4 mg. A micro-balance was used for all weighings. Residues left in the boats after combustion were weighed and their weights found to be in good agreement with those of ignition products obtained elsewhere, indicating that no loss of tungstic oxide had occurred, despite the large flow-rate of oxygen.

Precipitates that contained cinchonine, being appreciably hygroscopic, were left to settle to constant weight in a closed vessel containing some saturated calcium nitrate solution (50% relative humidity), in order to avoid increases in weight while portions were being weighed out. The platinum boats used in the experiment and in the corresponding blank run were similarly treated, and the flow of oxygen was stopped while boats were being placed in the combustion tube.

Results for carbon and hydrogen were corrected for the amounts of moisture absorbed by the complexes before analysis. Purified cinchonine was used as a standard for the analyses. (Found: C, 77.7, 77.8; H, 7.56, 7.53. Calculated for $C_{19}H_{22}ON_2$: C, 77.5; H, 7.53%.)

(v). Determination of nitrogen in tungstophosphate complexes

The Kjeldahl micro-procedure was used for the analysis of samples containing about 10 mg of organic material, which were digested in 30 ml flasks with 2 ml of sulphuric acid and the potassium sulphate - mercuric sulphate - selenium (32:5:1) catalyst advocated by Belcher and Godbert (48).

TABLE XXII

DETERMINATION OF NITROGEN IN CINCHONINE
BY THE KJELDAHL PROCEDURE

$C_{19}H_{22}ON_2$ = 9.52% of N

Volume of sulphuric acid, ml	Weight of catalyst, g	Extent of heating	Nitrogen found, %
3	3	18 hours, gently *	8.73
3	2	18 hours, gently	9.36
3	2	18 hours, gently	9.42
3	2	18 hours, strongly †	9.04
3	1	18 hours, gently	9.36
3	0.5	18 hours, strongly	<6.5

* Heated "gently" - at a temperature short of refluxing of the acid.

† Heated "strongly" - at a temperature where refluxing occurred. This varied with the concentration of catalyst in the acid.

In the subsequent distillation process, ammonia was collected in 5 ml of 2% boric acid solution and titrated with standard 0.025N hydrochloric acid, added from a calibrated micro-burette, in presence of methyl red and bromo-cresol green indicator. The acid had been standardised on the macro scale by means of borax.

Purified tri-n-butylamine, the volatility of which was so low that it could be weighed out in minute glass beakers which were transferred to the Kjeldahl flasks, and recrystallised cinchonine were used as standards. No difficulty was experienced in obtaining satisfactory results for nitrogen in tri-n-butylamine, but erratic results were obtained with cinchonine. The first promising result for the latter was obtained when 3 ml of sulphuric acid and 3 g of catalyst, which is relatively twice the amount used by Belcher and Godbert, were used. Ribas and Vázquez-Gesto (49) claimed complete break-down of cinchonine in 30 minutes, when somewhat similar conditions were used. However, it soon became apparent that the high temperature, obtained by vigorously boiling a mixture containing so much potassium sulphate, was leading to pyrolytic loss of nitrogen (50), and less had to be used or else a longer digestion given at lower temperature. As a result of a number of experiments with 10-mg amounts of cinchonine, details of which are given in Table XXII, it was decided to use 1.5 g of catalyst with 3 ml of sulphuric acid and digest mixtures overnight without too vigorous heating or refluxing of the acid.

Under these conditions, nitrogen was determined in tri-n-butylamine and cinchonine in presence of 40 mg of tungstophosphoric acid. Results were corrected for a small blank. (Found: N, 7.58, 7.57. Calculated for

$C_{12}H_{27}N$: N, 7.56. Found: N, 9.29, 9.25. Calculated for $C_{19}H_{22}ON_2$: N, 9.52%.) Results for nitrogen in cinchonine complexes were corrected for the low recovery of nitrogen obtained with cinchonine.

(vi). Standardisation of hydrochloric acid

Hydrochloric acid used for silver reductor and cellulose column experments was standardised, where necessary, by titration against borax with methyl red and bromocresol green as indicator.

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